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2nd International Symposium on ENVIRONMENTAL GEOCHEMISTRY

including 3rd International Symposium on Environmental Geochemistry and Health and 9th European Meeting of The Society for Environmental Geochemistry and Health

ABSTRACTS

(ed. O. Selinus)

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During recent decades there has been increasing interest in studying the interaction between the environment and geochemical qualities and processes. Variations in contents and natural distribution of chemical elements are significant when estimating the tolerance in environment and health to different forms of anthropogenic influence.

Geochemistry plays a successively increasing role in environmental research on a local as well as a global scale. Therefore it is of great importance to have a forum for researchers in this field, and we hope that this symposium will establish effective communication between geochemists as well as giving the state of the art.

The aims of the 2nd ISEG meeting are to present and discuss current research associated with natural and man-made environmental effects on soils, vegetation, waters and health.

We have received a large number of contributions for the symposium. The quality of the contributions is high and it is exciting to see the many interesting papers which are to be presented both orally or as posters. The scientific committee has had a challenge in compiling the papers into an interesting program, and I hope we have succeeded.

The scientific committee consists of the following people:

Dr Olle Selinus, Geological Survey of Sweden (chairman)
Dr Mats Aastrup, Geological Survey of Sweden
Dr Jan Byman, Swedish Environmental Protection Agency, Stockholm
Dr John Ek, Geological Survey of Sweden
Dr Ron Fuge, University College of Wales, Aberystwyth (representing the Society for Environmental Geochemistry and Health)
Prof Dr Gunnar Jacks, Royal Institute of Technology, Stockholm
Prof Dr Ulf Qvarfort, University of Uppsala
Prof Dr Kaj Rosen, Swedish University of Agricultural Sciences
Prof Dr Iain Thornton, Global Environmental Research Centre, London, Great Britain (representing the International Association of Geochemistry and Cosmochemistry)

We hope to offer you a successful meeting of high scientific quality and are looking forward to seeing you.

Dr Olle Selinus
Chairman of the Scientific Committee

SPONSORS

It would have been impossible to arrange a symposium of this size without sponsors. Therefore we would like to thank our sponsors for their different kinds of help in financing the symposium:

Geological Survey of Sweden
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HYDROLOGICAL MODELLING AND WATER MANAGEMENT IN A FORESTED AND CULTIVATED AREA USING A GEOGRAPHICAL INFORMATION SYSTEM

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University of Hamburg, FRG

The loss of natural watercourses and increase of water pollution makes the need for hydrological management obviously. A hydrological management including environmental aspects is necessary in rural areas where especially small streams are often intensely influenced by land - use.

This contribution shows a conception for hydrological management for a land area under forest and agriculture use north of Hamburg, Germany. The research was initiated by the Umweltbehörde Hamburg. The conception bases on field data. The hydrological management intends to decrease run - off from the area to a lower level. In areas under forest streamflow will be minimized. For areas under agriculture use compromises have to be accepted.

By using a geographical information system (GIS) spatial data are connected and interactions between them are shown. The effects of different kind of land - use on water balance and water quality are shown, also the results of changes in water balance on use.

The interpretation of available site dates (esp. soil, vegetation) was combined with mapping the streams in the area. The results show a needed improvement for many sites. Especially in areas with smaller watercourses (ditches) an improvement of their shape is necessary.

Research was done on representative sites to get more information about the water balance. This included soil mapping, profile analysis, measurement of water tables in streams and

groundwater, analysis of water chemistry and climatological measurements. The results show the intense drainage effect of artificial streams and ditches and the influence of water chemistry on site quality.

Decrease in run - off leads to larger water retention in soil and streams. This can be connected to larger retention of water pollutants. In agricultural areas the amount of nitrogen (as nitrate) in streams caused by fertilization is often high. Larger water retention can lead to a higher rate of denitrification. By laying out or restoring areas for higher water retention in the landscape (swamps,wetlands) the conditions for denitrification can be improved. The greatest effects can be expected in areas with high nitrogen loads in the streams. This often was found in outfalls from arable land. Here the concentration of nitrate reaches a concentration up to 50 mg/l. The nitrate concentration in fallouts from grasslands and forests is low.
The total loads supplied to the larger streams are investigated by the run - off coefficient. The effect of nitrogen retention as result of water retention is estimated from results of soil analyses on typical sites.

By using the GIS the effects of change in water balance on environment and land use in the area will be estimated. Different variations of management are simulated and the effects on the sites are shown, so the best design for land use planning can be pointed out.

ANTHROPOGENIC SURPLUS OF PHOSPHORUS AND NITROGEN IN SWEDISH RIVERS

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Many fresh waters as well as many marine waters, especially coastal zones, are enriched with the plant nutrients phosphorus and nitrogen. The effects are well known and in many cases unacceptable in the long run. Large and costly efforts have been taken to decrease the deterioration of the waters. This has created a need for more differentiated background concentrations to be used to estimate the anthropogenic surplus of phosphorus and nitrogen in the external load of these nutrients.

The phosphorus in our soils, rivers, lakes and seas originate from the bed-rock and becomes available to the growing plants primarily through weathering and secondarily through mineralization processes.

The nitrogen has its origin in the atmosphere. Present storage of nitrogen in the natural soils has been built up during hundreds or even thousands of years.

It seems reasonable to assume, that the leaching of phosphorus and nitrogen under pristine conditions is mainly associated with organic matter, either in dissolved or in particulate form.

The methods used to estimate the surplus of nutrients in any river or lake are based on: (1) TN/Si- and TP/Si-ratios with the global river mean as a fixed reference, (2) TN/C- and TP/C-ratios with the soil conditions as a principal reference, and (3) actual concentrations of TN and TP in undisturbed reference areas with the amount of humic matter, particulate matter, and pH as modifying factors. The use of Si as a general reference element is based on the assumption that the element has in principle no anthropogenic sources. One drawback is that the concentration of the element is dependent on the biological activity and nutrient sinks in the drainage basin.

Using the Si-ratios we can conclude that the Swedish rivers contain 65 % and 400 % more phoshorus and nitrogen, respectively, than the rivers of the world. In areas with high agricultural activity and large population density the excess is 450 % and 1900 % respectively, while corresponding figures for forested areas are 20 % and 75 %.

ENVIRONMENTAL GEOCHEMISTRY OF GROUNDWATER AND ITS IMPACT ON HUMAN HEALTH - A CASE STUDY

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ABSTRACT

To study the geochemistry of groundwater in parts of Central Ganga basin i.e. Aligarh city and its impact on human health, samples were collected from multiaquifer system and chemically analysed. Analytical data suggests that the trace metals like Fe, Cu, Mn, Cd, Pb and Cr are higher in concentration only in case of shallow groundwater, than the prescribed limits of World Health Organisation (1984). Further, to investigate the effects of the above metals on human health a survey was conducted with reference to the drinking water source and occurence of disease in the region. Some statistical data regarding type of disease were also collected from the concern department. Data emerging from the survey clearly indicate that there is a positive correlation between the efficiency of heavy metals and their impact as Gastro Intestinal Tract problems e.g. vomiting, diarrhoea, nausea, pain in the abdomen, passage of mucus, pus and blood in the faeces, burning empty stomach etc. The above diseases are occuring about 17 to 22% in the area where shallow groundwater with higher levels of heavy metals in under use while it is only 8 to 12% in the areas where deep groundwater is used as drinking water source.

OVERVIEW OF ENVIRONMENTAL GEOCHEMISTRY AT THE BRITISH GEOLOGICAL SURVEY

J.D.Appleton, T.K.Ball, W.M.Edmunds, D.G.Jones, P.J.Hooker, P.D.Roberts, P.R.Simpson, G.M.Williams; British Geological Survey

The poster presentation illustrates British Geological Survey involvement in the following aspects of environmental geochemistry :

1. Application of geochemical maps
    - 1.1 Heavy metals in the surface environment
    - 1.2 Heavy metal contamination from base metal mining and mineralization
    - 1.3 Animal health
    - 1.4 Land use planning
2. Hydrogeochemistry and health
    - 2.1 Trace elements in groundwater : fluorine
    - 2.2 Geochemical controls of water chemistry : attenuation of pollution in aquifers
    - 2.3 The unsaturated zone : a natural defence against toxic metals
    - 2.4 Indicators of agricultural pollution
    - 2.5 Acid rain : distribution of acid waters in the UK
3. Towed seabed gamma-ray spectrometry
    - 3.1 Methodology
    - 3.2 Geological mapping
    - 3.3 Distribution of artificial radionuclides from the Sellafield Plant in the Irish Sea
    - 3.4 Seabed radiometry of Imuruan Bay, Palawan, Philippines
4. Natural background radioactivity and radon
    - 4.1 Background radioactivity in the UK
    - 4.2 Radon potential mapping
    - 4.3 Radon hazard in geothermal and volcanic areas
5. Fluid processes
    - 5.1 Migration of radionuclides
    - 5.2 Generation and migration of gases (methane) in the subsurface

REGIONAL GEOCHEMICAL MAPPING IN DEVELOPING COUNTRIES AND ITS APPLICATION TO ENVIRONMENTAL STUDIES.

J.D.Appleton, D.M.A.Flight, J.Ridgway; British Geological Survey, Keyworth, UK.

Regional geochemical mapping surveys designed to identify mineral deposits have been carried out by the British Geological Survey in many developing countries, including ODA sponsored surveys in N.Sumatra, Kenya, Zimbabwe, Solomon Islands, Sierra Leone and E.Bolivia. In Great Britain and other developed countries, regional geochemical maps showing the surface distribution of trace elements have been used for environmental studies as they indicate (1) background trace and major element levels for natural uncontaminated geological settings, (2) pollution by mining and smelting activities and (3) areas with trace element deficiencies or excesses that could prejudice animal and human health. Geochemical mapping has identified areas with high levels of As, Cd, F, Mo, Pb and U associated with mineralization and mining activity that may produce natural or anthropogenic poisoning of vegetation and animals. In addition, molybdenum induced clinical or subclinical copper deficiency in cattle has been related to black shales with anomalously high Mo. Environmental pollution is now a subject of international concern yet in most developing countries there is no comprehensive data on the background levels of metals in the environment. Without these data, planners and other government authorities cannot monitor chemical changes in the environment that may have animal and human health implications.

The application of regional geochemical mapping to environmental studies in developing countries was investigated through a re-interpretation of regional geochemical data sets from E. Bolivia, N.Sumatra, Solomon Islands, Swaziland, Kenya, NE Zimbabwe, and Sierra Leone. This indicated that regional geochemical data collected for mineral exploration purposes have environmental geochemistry applications. One of the problems with mineral exploration geochemical surveys is that environmentally important elements such as Cd, Se, F and I are rarely determined. Investigation of the effects of sample density reduction through sample selection suggests that in many cases significant geochemical patterns can be detected through the analysis of a relatively small sub-set of samples from sample archives, thus providing significant savings over re-analysis of all samples or low-density resampling. The effectiveness of different sampling media, including drainage sediment, soils and water, for regional environmental geochemical surveys are compared.

The relevance of regional environmental geochemical maps for land use planning is investigated by comparing regional geochemical data from the Solomon Islands and N.Sumatra with results of land resource surveys.

Regional geochemical mapping is a rapid, cost-effective and reliable method of providing a comprehensive data base on the background levels of metals in the environment that will permit governments to monitor environmental degradation, environmental pollution and to investigate trace element linked degenerative diseases in crops, animals and humans.

GEOENVIRONMENT - RELATED DISEASE ENDEMICITY IN EASTERN AFRICA

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The endemicity of some diseases in eastern Africa is attributable to the abundance of certain trace elements in the geoenvironment . The prevalence of goiter (about 60 %) and cretinism in the highlands of Tanzania and Kenya , is a consequence of the low level of intake of iodine (about 25 µg per capita per day , which is one-sixth of the recommended intake). These areas are characterised by high elevation , deforestation and severe soil erosion . Since the soil humus is the principal repository of iodine (in the form of humic complexes), the removal of soil humus due to erosion leads to depletion of iodine in the soils and waters , and food grown in such soils . Besides , such communities live far from the coast , and hence do not have the oppurtunity to ingest iodine by being exposed to sea-generated , iodine-bearing aerosols . Iodine Deficiency Disorders (IDD) of high severity can be ameliorated through the use of iodinated oil either orally or through injection (at a cost of USD 0.09 per capita per annum). Moderate IDD can be ameliorated or IDD could be prevented through the use of iodinated salt (at a cost of USD 0.05 cents per capita per annum).

The endemicity of dental and skeletal fluorosis in parts of eastern and southern Africa is traceable , in the ultimate analysis , to the volcanics of the East African Rift . The fluorosis in northern Tanzania is attributed to the drinking of highly fluorous waters (with more than 10 mg / l of fluoride), and the use of " magadi " (sodium bicarbonate encrustations with about 1000 ppm of fluoride) as salt . Recent studies have drawn attention to the possibility of some metabolites becoming carcinogens when OH^- is replaced by F^- .

The highest incidence of stomach and liver cancers in Tanzania is to be found in the areas of northern Tanzania which witnessed Quaternary and Recent volcanism . High gastric cancer mortality has been reported from countries as diverse as Japan , Chile , Costa Rica , Iceland , etc. The common factor among all these countries is the existence of Recent volcanism. The incidence of stomach cancers appears to be related to the ingestion of N-nitroso compounds which are known to be carcinogen initiators , and whose genesis could be traced to volcanic emissions of NO_x .

The phosphorite of Minjingu , northern Tanzania , is radioactive (with about 200 ppm of uranium on the average). Thermoluminiscence dosimeters have been employed to measure the radiation doses to which persons employed in mining , milling, transport and application of phosphorite, are exposed . The doses recorded are less than 4 mSv / month . Though no adverse health consequences are recognisable in the short term , the long term consequences of such radiation exposure needs to be monitored .

BEHAVIOUR OF SCANDIUM AND BARIUM IN SOIL SOLUTIONS AND GROUND-WATER: POTENTIAL USE FOR WEATHERING STUDIES.

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The geochemistry of Sc and Ba have been poorly studied, especially in soils. They are dispersed elements, rarely forming specific minerals. Sc^{3+} can replace Fe^{2+} in silicates (1) and is more abundant in pyroxenes and clays. It forms hydroxy-complexes in water. Ba^{2+} can replace Sr and Pb in feldspar minerals (2). Relatively high (.8%) contents are found in granites (4). In water, its solubility is generally controlled by SO_4 (3).

Material and methods :

7 experimental sites representing the major lithologic types of the Roman part of Switzerland have been choosen at an altitude of 900 to 2000 m. Bedrocks are: limestones, gneiss, molasse, flysch. Soils are brown soils, lithosols, podzols...

In each of these sites, rain, snow, soil solutions and spring waters are sampled. Rain and snow are collected with polyethylene funnels. Soil solutions draining representative soils are obtained by 0-tension lysimeters made of hard Polypropylene gutters inserted parallely to the slope at the bottom of undisturbed soil. In the molasse site (LRY), porous cups were added to sample capillary fluxes. Cold springs draining each area were selected for their relative chemical stability. Samples were collected during a year, after each major rain or snowmelt event. After filtration, samples were analysed for a large set of elements using an ICP-MS (VG Plasmaquad)

Results:

Ba is one of the major trace element in soil solutions wereas Sc is the 7th in order of importance. Compared to those values the concentrations existing in rain and snow are very low and generally neglectible. So Ba and Sc are produced in the soil itself. In this environment Ba and Sc exist in soluble form (smaller than .45 µm) probably as aqueous complexes (1).

Sc is strongly correlated in soil waters with Si: In 4 sites, r^2 is higher than .88 and for Lry it equals .74.

In the Karstic regions there is no correlations between Sc and Ca or Mg which proves that Sc doesn't come directly from limestones. The important Sc content of clays (25 ppm) can be the origin of the correlation.

Ba is also more correlated with Si than with any other element even with a lower r^2 (.61 to .85) than for Sc-Si. It is interesting to notice that the level of Ba is lower in springs than in soils, showing an accumulation along it's pathway, wereas Sc remains more stable.

Conclusions:

Scandium and barium originate from different type of minerals. Both seem to be exported out of the soils with Si. As the Sc/Si or Ba/Si ratios are not the same in rocks, the Sc/Si ratio in soil solutions could be used as a tool for the assessment of mineral weathering rates.

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THE ESTIMATION OF THE NATURAL PROTECTION OF GROUNDWATERS OF THE BYELORUSSIAN POOZERJE AREA FROM THE NITRATE POLLUTION

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A constant nitrate pollution of groundwaters in the Poo - zerje area has resulted in the disturbance of the equilibrium and the loss of the selfpurification capacity of the natural environment.

Spatial anomalies of the technogenic flows including nitrates are consequences of the interaction between landforms and dynamics of soil and groundwaters. The mozaic pattern of technogenic flows depends on a nonuniform distribution of the filtration and physical-chemical properties of filtering and water-bearing rocks. The structure of technogenic flows is a function of the transfer forms: mechanical, biological and physical-chemical ones.

The mechanical form of the transfer is more distinctly shown within developed landscapes; biological one - in the soil cover; physical-chemical one - in rocks of the aeration zone and water-bearing horizons . The domination of one or another form of transportation depends on the state of the geological environment and climatic conditions of the studied region.

The analysis of litho- and hydrogenesis of the Byelo - russian Poozerje territory shows that groundwaters are not protected from any technogenic pollutions. E.g., the for - mation of the groundwater chemical composition occurs under conditions of humid climate. Such conditions are characterized by the domination of processes of hydrolysis , leaching, dissolution. The area of overmoistened lands in the Poozerje region constitutes more than 50 %. Concequently, the formation of soils as a biological barrier occurs under conditions of the land overmoistening. Considering a high mobility of nitrate compounds none of the natural barriers is efficient. Flat, bogged lands, and thermokarst depressions are mostly susceptible to technogenic attacks. Besides, the capacity of nitrate compounds to form comp - lex combinations creates new physical-chemical conditions for the migration of macro- and microelements.

VARIATIONS IN WEATHERING PROCESSES AND RATES WITH TIME IN A CHRONOSEQUENCE OF SOILS FROM GLEN FESHIE, SCOTLAND

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Chemical and mineralogical characteristics have been determined for a chronosequence of six soil profiles developed on river terraces derived from schists in the western Cairngorms area of Scotland. The fluvial surfaces on which the profiles have developed have been dated at 13000, 10000, 5500, 3500, 1000 and 80 radiocarbon years BP using quantitative soil stratigraphic data and various methods of absolute dating. The profiles less than 10000 years old are mineral alluvial soils whereas the two oldest profiles are humus-iron podzols. The C horizons are very similar chemically and mineralogically, and the soils have similar pedogenetic histories.

Exchangeable Ca and Mg decrease with time, but the most marked trend in the exchange complex is seen in base saturation which decreases exponentially from 24.6% in the Ah horizon of the youngest profile to 2.8% in the comparable horizon of the 10000 year old profile according to the chronofunction $y = 3.448 + 22.621 \exp(-0.0008072t)$ where y is the % base saturation and t is the age of the profile. Long-term weathering rates of base cations, calculated from the loss of these cations relative to Zr which is considered to be a stable immobile element, also appear to decrease exponentially with time, but this seems to be an artefact of the calculation which is based on averages over periods of time ranging from 80-13000 years. The magnitude of loss of base cations from the profiles decreases in the sequence Na>K>Mg>Ca but the mobility of the loss is in the order Mg>Na>Ca>K reflecting the dissolution of chlorite and loss of Mg, and the more rapid weathering of plagioclase feldspar (particularly in the coarse sand fraction) than K-feldspar. The clay fractions, although <2% of all horizons, also show distinct patterns with age in that chlorite and mica are less abundant in older soils and vermiculite is more abundant, the latter phase often having hydroxyaluminium polymers in the interlayer region. The differences between profiles are due to duration of weathering.

All of the temporal trends observed have important implications for the acidification of soils in the Glen Feshie area.

DIGITAL MODELLING OF ADMIXTURES TRANSFORMATION IN THE ATMOSPHERE OF THE MOUNTAIN BASINS

A.Baklanov, S.Mazukhina (Apatity, Kola Science Centre)

The economical development of mountain territories and building of industrial enterprises in areas with complex orography require particular researches of possible negative aftereffects on the environment. In similar conditions, the changes of winds regime and microclimate in mountain valleys and circuces influence much the spread of pollutant admixtures in the atmosphere. That's why the first stage of work comprises calculation of speed fields and turbulent characteristics in the examined area on the basis of the digital model of the atmosphere dynamics in the situation with the complex orography /1/. On the basis of these data the spread of gaseous emissions in the air calculated.

The atmosphere of mountain circles, basins and quarriesis a closed system,that has limitad air-exchange with the environment and often there occur calms, in-vrsions and fogs, that's why the studies of possible chemical transformation of the admixtures components in the atmosphere are very important when model-ling the processes of the atmosphere pollution with industrial emissions.In this connection, on the basis of physical-chemical modelling /2/, the model of the atmosphere admixtures spread in conditions of complex orography is comple-ted with autonomous studiesof some mechanics of pollutant admixtures transfor-mation.

The purpose of these studies is to determine the possibility of the spread of new toxic products frpm the second pollution of the atmosphere. In particular, since there's free oxigen in the atmosphere, it presents a system /atmosphere/ that can provoke acidification process, so, practically all of the sulphur and nitrogen interaction form sulphates and nitrates as the extreme form of acidi-fication and this fact proves the possibility of acidic precipitations when in-teracting with water. The Gibbs method of free energy minimization was used for studying of gases behaviour in the air (photochemical factor not considered). The above mentioned method allows studying of systems, consisting of electrolytes solutions, gas and condensed phases.

There have been accomplished some computer made calculations of the pollutant admixtures spread and nitrogen/ sulphur oxides transformation for gaseous and condensed phases concerning "PechengaNickel" plant, near the Soviet-Norwegian border; Kirovsk hydro power station near the Khibiny mountains and Udokanski mining concentrating plant in Chara basin. The mechanism of temperature stratification influence on the nature of mountain ranges streamline process with wind flow.

There has been demonstrated the formation of separate recicle flows zones in the atmosphere of mountains valleys. In these zones, there is an active mixing of pollutants in the conditions of equilibrium stratificated atmosphere. As there is an inversion, there is a considerrable attenuation of exterior large flows in mountain basin and the admixtures are accumulated up to rather high level in (the zone of industrial emissions) in the

nr&ar-earth atmosphere layer in the inferior part of the basin.

The calculations pf the sulphur oxides and nitrogen oxides transformation in the atmosphere of Chara basin showed that, once an industrial emissions occured for the first 5 hours as a result of the interaction nitrogen oxides and nitrogen acid usually prevail in the air.

After 10 hours, H2S04 prevails and pH for precipitations varies within 4,9 and 3,7 during the liquid phase. This proves that there is a posibility for the process of active interaction of oxides with liquid and acidic precipitations, which lead to acidification of soils and water reservoirs.

Near the Kirovsk hydro power station there has been observed the formation of nitric and sulphuric acids. Neverthelass, the presence of the apatite-nepheline compound near the hydro power station as studies showed, neutralize considerab-ly the acidification of soils and wabers in the area.

N,P and K distribution in soils of different plant communities in wet evergreen forests of Silent Valley, Kerala

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Abstract

The Silent Valley National Park ($11^{o}05'$ to $11^{o}25'$N latitude and $76^{o}21'$ to $76^{o}33'$E longitude) on the Western Ghats, Kerala is bestowed with luxuriant wet evergreen forests (rainforests). The area enjoys a rainfall of 3000 mm annually and the altitude varies from 900 - 1200 m. The drainage is controlled by the river Kunthipuzha. Although the species diversity is high, dominance of certain plant communities is observed along large patches within the biome. Seven plant communities have been identified in an area of 30 km^2 and each holds the name of the first two dominant tree species:

1. Cullenia exarillata - Palaquium ellipticum, 2. Palaquium - Mesua ferrea, 3. Poeciloneuron indicum - Palaquium, 4. Mesua - Calophyllum elatum, 5. Mesua - Cullenia, 6. Ochlandra sp. (reed) -Calophyllum and 7. Ochlandra - Poeciloneuron. Investigations were carried out in soils of these plant communities. Five study plots, each of 50 x 50 m were laid out randomly in each plant community and three soil pits were taken from one plot. Samples were taken from 0-20, 20-40 and 40-60 cm layers of soil pits and composited for each plot. Analyses were carried out for total N, extractable P and K. It was found that N, P and K in 0-60 cm layer differed significantly in the seven plant

communities. Further, Multiple Comparison Among Means (MCAM) revealed that in the 0-60 cm, soil N in Cullenia - Palaquium, Palaquium - Mesua and Ochlandra - Poeciloneuron differed significantly from Mesua - Calophyllum, Mesua - Cullenia and Ochlandra - Calophyllum whereas soil P in Mesua - Cullenia showed significant difference from all other plant communities. It was also seen that soil K in Mesua - Cullenia differed significantly from Cullenia - Palaquium, Palaquium - Mesua and Poeciloneuron - Palaquium. Thus significant differences in N, P and K level in the soils from different plant communities were observed suggesting the influence of soil properties on vegetation characteristics. Further studies on the input and output of nutrients in these plant communities are warranted to understand the causes of different nutrient regimes.

CONTROLS ON THE REDUCING CAPACITY OF GRANITIC GROUNDWATERS

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We have used the concept of reducing capacity (RDC) to characterize the redox status of the shallow groundwater (depth<100m) on the island of Äspö, a small island 20 km north of Oskarshamn along the east coast of Sweden. The shallow groundwater of Äspö is strongly reducing with high concentrations of dissolved organic carbon and iron(II). The penetration of oxidizing surface water into hydraulically conductive fracture zones is the redox disturbance of interest. Thus we choose the standard potential of the O_2/H_2O redox couple as the endpoint for a hypothetical redox titration.

The dissolved components which are thermodynamically reducing with respect to our chosen redox endpoint are all aqueous iron(II) species (5×10^{-6} mol l^{-1}), and TOC (1.75×10^{-4} mol C l^{-1}). We assume an average redox state of C(0) for TOC, and a 4 electron transfer for complete oxidation to CO_2. In addition, we specifically include the reducing surface sites of biotite, present within the host rock. RDC is defined below with units of mol l^{-1}.

$$RDC = [Fe(II)_{(aq)}]_{total} + 4[TOC] + [Fe(II)]_{surface}$$

The contribution of TOC and dissolved iron(II) to the RDC in our redox titration gives 7×10^{-4} and 5×10^{-6} mol l^{-1}, respectively.

It is difficult to estimate the contribution of reducing surface sites because of the large uncertainty in wetted surface area (m^2 l^{-1}) for a fracture zone. The surface concentration of iron(II) for the host granite is calculated to be on the order of 1μmol m^{-2}. However, the geometric surface area of a granite face is small compared to the surface area of the pore space within the rock matrix. For the granite considered here, a rock face of $1m^2$ contains approximately 4×10^{-4} mol of surface iron(II) sites within a 1mm deep surface layer. This would give about the same reducing capacity as does TOC, for a 10cm wide fracture with 1% flow porosity confined between two such granite faces (2 m^2 l^{-1}).

Although the dissolved reductants are rapidly available for reaction, their contribution to RDC is small compared to the reservoir of iron(II) within the host rock. Constraints on the available aqueous RDC thus includes the diffusion depth into the rock matrix, renewal of reducing surfaces and release of structural iron(II) through chemical weathering, heterogenous chemical reaction between reducing surface sites and adsorbed oxidants, as well as slow oxidation of refractory TOC.

STUDY OF THE EFFECT ON THE SURFACE WATER AND SOIL QUALITY DUE TO SPILLAGE OF CRUDE OIL AND FORMATION WATER DURING DRILLING OPERATION IN RUDRASAGAR AREA,ASSAM,INDIA.

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At present in Rudrasagar area of district Sibsagar,Assam (94° 35′ to 94° 41′ E; 28° 59′ to 37° 59′ N), exploration of crude oil is under operation. During the process of drilling and oil collection disposal of large scale formation water with high salinity, spillage of crude oil at drilling sites and oil collecting stations used to take place. As a result the soil/water system degradation has been observed in the surrounding areas of Rudrasagar oil fields.

To assess the level of contamination we took up this study and collected 50 water and 50 soil samples from 20 selected locations in three different seasons during March 1990 to February 1991. Chemical contamination parameters have been analysed to estimate the soil/water quality for agricultural and domestic use. The common parameters with regard to water quality viz.pH,D.O.,C.O.D.,T.D.S.,oil and grease were estimated by standard methods. It is indicated that the dissolved oxygen has decreased and chemical oxygen demand has increased in water at few locations.Moreover,surface water contains oil&grease,nitrate, nitrite,sulphide and ammonia above permissible limit. Toxic metal trace elements namely - Cr,Ni,V,Pb,Hg,As,& Cd were estimated by Atomic Absorption Spectrophotometer using flame,electrothermal and hydride generation system for both water and soil samples. Suitable digestion and preconcentration techniques were applied whenever necessary before measuring the metal concentration.

The toxic metals viz. Ni,V,Cr,Pb, are present in the mg/L range,while Hg,As,Cd,occur in micro gramme/L range.From this study it is quite evident that overdose of spillage from drilling operation have taken a serious turn and has become major health hazard.

A FLOW INJECTION METHOD FOR ALUMINIUM SPECIATION IN NATURAL WATERS, AND A COMPARISON OF THIS METHOD WITH A RELATED MANUAL METHOD

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As a result of acid precipitation, the concentration of aluminium in natural freshwaters has increased. Different forms of aluminium are poisonous to different degrees, so it's important to know their concentrations.

Three of us (NC, L-GD and AS) have worked on the development of a Flow Injection method for aluminium speciation (Clarke et al, 1991). Aluminium reacts with oxine (8-hydroxoquinoline) at pH 5.0. The reaction is terminated by extraction into chloroform. The reaction time is about 2.3 s, much shorter than that used normally. After separation, the amount of aluminium trioxinate in the organic phase is determined spectrophotometrically. The detection limit is about 5 µg/l. We can make up to 60 measurements per hour.

The system has been validated using model substances with known complexation constants. Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$, aluminium's sulphatocomplexes and to some extent some of its weakest organic complexes are included in the measured fraction, whereas fluorocomplexes, citratocomplexes and $Al_{13}O_4(OH)_{24}^{7+}$ are excluded. In order to study the behaviour of aluminium's complexes with Nordic Reference Fulvic and Humic Acids in our system, we have used equilibrium dialysis. Our results show that these complexes are excluded from the measured fraction.

Many other methods for aluminium speciation exist. Among the most widely used are those of Barnes (1975), Driscoll (1984) and LaZerte (1984). These involve the reaction of aluminium with oxine, with subsequent extraction at pH 8.3 into methyl isobutyl ketone. Driscoll extended the method by using a cation exchange column to separate non-labile monomeric aluminium from labile forms. Atomic absorption was used by all three to measure the aluminium concentration in the extract.

One of us (MB) has worked with a method based upon these. With this method, Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$ and the fluorocomplexes were measured as labile monomeric aluminium, while the citratocomplexes and complexes with Nordic Reference Humic Acid were measured as non-labile monomeric aluminium.

By combining these methods, we can divide monomeric aluminium into three classes, including the hydroxocomplexes, the fluorocomplexes and the most important organic complexes, respectively. This may be important when trying to correlate a certain measured concentration with, for example, fish death.

We have also studied the results of soil leaching experiments with both methods.

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GEOLOGY OF THE CENTRAL MIDCONTINENT AREA OF THE UNITED STATES OF AMERICA AND RADON LEVELS MEASURED IN RESIDENTIAL HOMES.

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During the last five to seven years, natural and man-made radon pollution has received a large measure of attention by the United States Environmental Protection Agency and subsequently by health departments or similar agencies in the individual states. Natural pollution caused by the anomalous concentration of parent and daughter elements of U-238 in the earth's crust above levels considered to be safe to man's existence, is the result of a number of complex geological, geochemical, and physical processes. In order to safeguard the public against the effects of radiation and to aid in planning, many attempts have been made to predict levels of radiation in various geological environments. Mixed results in this endeavor are due to our incomplete understanding of the behavior of the critical radionuclides.

Studies of radon levels in residential homes in the central midcontinent area of the United States show that 25 percent commonly have concentrations larger than the recommended safe level of 4 pCi/l. Since uraniferous rocks are the ultimate source of radon generation, an understanding of their aerial extent and the concentration of radionuclides within them is important. Tertiary, Cretaceous, Pennsylvanian, and Mississippian rocks are the major bedrock units underlying this area. Unconsolidated to partially consolidated sands and gravels, together with lesser amounts of volcanic ash and fresh-water limestone make up the Tertiary rocks. Anomalous uranium concentrations up to 150 ppm in locally developed silcretes occur in these rocks. Cretaceous rocks consist mostly of marine chalk, limestone, and shale, together with nonmarine sandstone. Anomalous uranium concentrations occur in parts of the widely distributed, organic-rich, black, clayey Pierre Shale, and in organic-rich portions of sandstone channels and possibly lignite beds in the Dakota Formation. Pennsylvanian rocks are characterized by cyclically occurring, partly marine and partly nonmarine, thin limestones and dolomites, shales, sandstones, and coal. About eighteen, thin, organic-rich, black shales underlie thousands of square miles in the midcontinent. They are 0.5-1.0 m thick, but they occur repetitiously every 15-50 m. They commonly contain from 20 to 200 ppm uranium, but reach concentrations as high as 700 ppm. The Mississippian marine succession generally starts with dark shale followed upwards by a thick sequence of carbonates and terminating with a mixture of shales, sandstones and carbonates. Except for the shale, no potential anomalous radioactive element concentrations are to be expected. There is evidence that major deep-seated faults or terrains that are heavily fractured may provide pathways for radon to rapidly migrate to the surface. However, a direct correlation between radon levels measured in homes in the central midcontinent and the concentration of radioactive elements in the soil or bedrock is far from perfect.

GEOCHEMICAL EXPLORATION DATA : UTILITY IN ENVIRONMENTAL STUDIES

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Abstract

Everincreasing industrialisation and its impact on environment is a major global problem. The growing concern in this regard necessiates integration of various types of chemical data in understanding environment in general and pollution in particular. One of the efforts in this direction is to utilise geochemical exploration data, generated with the purpose of delineating potential mineral deposits, in the environmental assessment studies like water quality, soil contamination etc. The idea of relating geochemical survey data to such environmental pollution studies is still in the infantile stage, particularly in the third world countries.

Geochemical exploration data, obtained during various geochemical surveys using soil, water etc. as media from different parts of Rajasthan, has been utilised in evaluating local environmental problems. Soil survey carried out near Debari Hindustan Zinc Smelter in Udaipur district has shown that the anomalous concentrations (approx. 1000 ppm) of Zn in soil are neither from the underlying rocks nor from any mineralisation, but contributed from an artificial source, possibly from Hindustan Zinc Smelter, in the form of ash or dust. In a similar survey near Goj in Banswara district anomalous Zn values were noted in soil (ranging from 240 to 4800 ppm) and ground water

(0.01 to 0.85 ppm) samples. The presence of high Zn values in two media indicate the presence of low grade Pb-Zn mineralisation in the area. But, these values also indicate that a natural source for contamination of ground water and soil exists in the region which should be taken into consideration while using ground water for drinking and irrigation purposes. Similar observations are also recorded from the soil surveys carried out in Pur-Banera base metal mineralised belt in Bhilwara district where Cu,Pb & Zn range from 36 to 18700, 06 to 37200 & 106 to 16300 ppm respectively and in Umra area in Udaipur district where the above metals range from 158 to 2680, 06 to 140 & 280 to 6630 ppm respectively.

Pollution, whether natural or artificial has to be taken into account keeping in view the toxic effects of these metals particularly Pb. Some remedial measures have to be evolved after conducting a detailed study in the areas mentioned above to minimise the possible long term effects on inhabitants. In future, geochemical surveys therefore, have to be planned and executed keeping environmental aspect in view.

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POLLUTION BY ARSENIC AND MERCURY IN FLUVIAL AND LACUSTRINE SEDIMENTS

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The Tuy River and Lake Valencia drainage basins, located in north-central Venezuela, were selected to conduct a geochemical study in sediments with the propose of establishing the alteration of the natural background of arsenic and mercury as a product of all the human activities taking place in those two heavily populated (> 600 persons/Km^2) watersheds.

The bottom sediment samples (86) used in this study were collected in the Tuy River (39) and Lake Valencia (22 fluvial and 25 lacustrine), whereas the all fluvial particulate samples (61) are from Tuy River drainages. Arsenic and mercury were determined by atomic absorption spectrometry by using a hydride-cold vapor system.

The analytical results obtained for mercury permitted to establish the natural background concentratation for the Tuy River (54 ug/Kg for the bottom sediments and 240 ug/Kg for the fluvial particulates) and for the Lake Valencia (110 ug/Kg for both fluvial and lacustrine sediments) basins. The average concentration values estimated for the polluted samples were: 150 ug/Kg and 610 ug/Kg for the bottom and suspended sediments from the Tuy River and 1000 ug/Kg and 560 ug/Kg for the fluvial and lacustrine sediments from the Lake Valencia basin, respectively. These results show that the Lake Valencia presents higher degree of pollution than the Tuy River drainage and that the fluvial particulates permitted to detect a larger number of polluted samples.

Arsenic was only determined in the sediment samples from the Tuy River basin. The natural background concentration found for arsenic was 0.60 mg/Kg for the bottom sediments and 2.9 mg/Kg for the fluvial particulates. The polluted samples yielded an average concentration of 2.0 mg/Kg for the bottom sediments and 7.2 mg/Kg for the riverine particulates.

The fact that more than 50% of the samples collected in the Lake Valencia and Tuy River watersheds showed pollution by mercury and arsenic is indicative of the influence that are exerting all the domestic, industrial and agricultural activities in the study area.

LONG-TERM CHANGES IN THE NUTRIENT POOL OF FOREST SOIL ORGANIC HORIZONS BETWEEN 1949/50 AND 1987

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Fifteen soil profiles form the Alltcailleach Forest, NE Scotland were first sampled in 1949/50 and resampled in 1987. The original soils were stored and each of the sites accurately relocated. The forest consists of old (19th century) and young (20th century) coniferous plantations. Previous studies have shown that soil chemical changes over the 37/38 year period are characterized by decreases in pH, base saturation and CEC and increases in extractable Al and SO_4.

Samples collected from the upper organic horizons of these soils have been analysed for total Ca, Mg, Na, K, P and N content following acid digestion. Long-term changes in total Ca and N are characterized by significant decreases in concentration between 1949/50 and 1987. Magnesium, K and P concentrations showed smaller decreases with time, although changes in the soils from the older plantations were more pronounced. In contrast to other base cations, Na showed a slight increase in concentration over the 37/38 year period.

Differences also occurred in the concentration of nutrients between the 2 types of plantation. Forest soil organic horizons from the older stands had lower concentrations of Ca, Mg, Na, K and P than soils from the younger plantations. The lowest concentrations of nutrients were found in the freely drained podzolic soils.

Between 1949/50 and 1987 increases in forest soil organic horizon thickness have resulted in an increase in the total amounts of nutrients stored in the forest floor. The increases in organic horizon thickness therefore largely override the decreases observed in nutrient concentration, in terms of nutrient pools, but not in terms of plant nutrient availability. Accumulation rates have also been calculated for each of the elements.

Decreases in the concentrations of essential nutrients such as N, P, K, Ca and Mg and their build up in thickening organic layers in the forest could be a considerable potential problem within the ecosystem. Accumulation of organic matter associated with soil acidification may ultimately lead to long-term nutrient deficiencies.

SPATIAL VARIABILITY IN BASEFLOW STREAM WATER CHEMISTRY WITHIN UPLAND CATCHMENTS

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The effects of soil type, parent material and catchment characteristics on baseflow stream water chemistry have been studied by investigating spatial changes in water quality along the length of streams from their source to the catchment outlet. Spatial sampling enables catchments to be regarded as a series of sub-catchments, steadily increasing in size and with a gradient of relative importance of dominant soil types. Individual catchments are each characterized by downstream chemical profiles, which show the relative importance of different geochemical inputs into the stream.

Data is presented from a number of chemically distinct upland catchments in NE Scotland, where the approach has been used. Samples were collected at 250-m intervals along each stream, which was sampled on 3 separate occasions. Samples were analysed for pH, Ca, Mg, Na, K, Al, TOC, Cl, SO_4 and NO_3.

Spatial changes from the source to the catchment outlet are characterized by an increase in pH, Ca and Mg. Changes in Na and K are less consistent, whereas Al and TOC concentrations tend not to change or show a decrease in concentration. Although SO_4 concentrations show no consistent trend, NO_3 shows a consistent decrease from the top to bottom of the catchments. This decrease may be caused by lower inputs of NO_3 from the more fertile soils at the bottom of the catchment or by uptake of nutrients by aquatic organisms. Superimposed upon these overall trends are clear fluctuations in solute ion concentration within individual catchments, which are reproducible between sampling events.

Chloride generally shows an increase in concentration down the catchment. If Cl is assumed to be entirely of atmospheric origin, changes in the base cation: Cl ratio can be used to assess the influence of changes in weathering inputs downstream. This provides an important means of relating the solute chemistry of drainage waters to the geochemistry of the soils and parent materials. The approach could also be used to provide an indication of groundwater inputs into catchments. Such inputs can be a major source of error in quantifying hydrochemical budgets.

Methodics of geochemical investigation of urban area; Example Central-Berlin

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Since more than ninety years, in the urban area of Berlin-Schoeneweide (7.7 km^2) dangerous and toxic substances have been used in the production processes of various industrial companies. The extensive emission caused by the industrial production leads to a variably high accumulation of toxic materials in the soil of the sourrounding area.
Soil samples were taken from a depth of 0 - 20 cm and analysed for main and trace elements as well as for TOC, pH value and electrical conductivity. More soplusticated, computeraided calculations of statistical parameters of the distribution of the single elements were done.
Corresponding to the types of primary land use as well as to the industrial and commercial use the total data base or parts of it have been evaluated.
The element distribution in the surface soil shows a clear dependence on the types of urban land use and typical production processes in industrial and commercial areas. In spite of the high degree of sealing as well as the density of population and industry, statements can be deduced about the migration behaviour of the elements and the laws of their distribution in the surface soil because of the high density of sampling sites. The overall univariant background (median) of the sands and gravels of the Berlinian Pleistocene watercourses is used as geogene or natural geochemical background for the Schoeneweide Area. Additionally the geochemical background of the urban area Schoeneweide already shows a certain accumulation of Cu-Zn-Pb-Hg-Ni-Sn, which is caused by anthropogenic influence. Compared to the KLOKE approximate values for cultivated soils, an anthropogenic load with the elements Pb, Cu, Zn and partly B is confirmed. The distribution of the contents of the elements

Ti and Zr prove their predominantly geogene or pedogene character (composition of the substratum). With increasing density of industry and population the values of the electrical conductivity also increase, parallel to the content and diversity of the elements. The industrial productions in the urban area Berlin-Schoeneweide are charaterized by Cu-Zn-Pb-Hg-Sn-Ni-emmissions, which caused the contamination of the surface soil.

The factor analysis, calculated in the frame of multivariate statistics, gives a decisive increase of knowledge of the migration of elements in the exogene geochemical field. Due to the principle effective causes, the polyelement factors can be subdivided into three groups:

1. Factors of the anthropogenic contamination (building metallic wastes and building materials --> Sr-F-La-Y-Ca, waste products --> Cr-Mg-Ni-Mn-Co, old loads --> As-Hg, anthropogenic influence, in generell --> electrical conductivity and Hg-As-TOC, green spaces --> Ag-Cd-P)
2. Environmental features with partly anthropogenic influence, indicating an element accumulation at biogeochemical and physicochemical (alkine) barriers (V-Be-Co-Al-Ba-Ti-TOC-Mo-Pb, Fe_{total}-Mo-Co-TOC, pH value-Ca);
3. Naturally caused factors (geogene, pedogene) with partly anthropogene influence, given informations of the quantity of the alkaline metals (Na-K-Rb-Al) as well as on tho composition of the substratum of the soils (Zr-Ti, Nb).

By cluster analysis (Q-Modus) the data array was splitted up into 20 classes. One class characterizes the regional geochemical multielement background of Schoeneweide and another on represents the local geochemical background with tendencies of acidification in the urban area Berlin-Schoeneweide. The most important types of anomalies Ag-Hg-Sb-As±Zn,Sn; Cu-Sn-EL; Cu-Zn-Cd; Cu-Sn-Sb-Zn-Cr-Pb-Ni-Cd; Cr-Ni-Mg-Mn charakterize the technogene immission influence as a result of the processing of raw materials in high-temperature processes (Berliner Akkumulatoren- und Elementefabrik, Berliner Metallhuetten und Halbzeugewerke a. o.) as

well as the accumulations of old loads in the investigated area. In all, 36 geochemical anomalies were indicated. Most of the anomalies have complex anthropogenic causes. At the same time, anomalies of TOC±Cu, Cd, Ag, Ni are distributed, which point to a partly organic bond of the heavy metals.

The Transfer of Organic Carbon from Forest Soils to Surface Waters

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Dissolved organic carbon is a common constituent of Swedish surface waters. The environmental significance of DOC for the mobilization of metals, for the bioavailability of metals and as source of acidity is increasingly well documented. Yet despite the prevalence and importance of DOC in streams and lakes, relatively little is known about the processes which control the transfer of terrestrial DOC to the aquatic environment. This shortcoming makes it difficult to assess how the changes already observed in surface water DOC are related to factors such as climate, land use and acidification, or to design appropriate strategies for managing the DOC content of surface waters and closely associated substances, including mercury.

The processes and pathways which control the amount and chemical character of DOC moving from forest soils to surface water were investigated using a hillslope oriented approach that integrates data on water flux through the soil, the distribution of DOC within the hillslope, and the chemistry of runoff leaving the hillslope to discern the dynamics of DOC export. Particular attention was paid to changes in the chemical character of the DOC from season to season and in response to increases in stream discharge.

The amount of carbon per hectare exported from the vicinity of the study hillslope was comparable to that coming from the mire at the head of the catchment. Even that relatively high export of DOC, though, was small relative to the storage of organic carbon in the catchment, indicating how tightly closed the terrestrial carbon cycle is. The potential for disturbances in that cycle to profoundly effect surface waters was evident from the positive relationship between both the amount and quality of DOC and water quality parameters, including acidity, aluminum content and aluminum speciation.

In the hillslope, the characteristic vertical pattern of decline in DOC and aluminum below the contact of the A and B soil horizons was accompanied by a lateral pattern of downslope increases in DOC and aluminum. These increases were paralleled by the steady accumulation of water from upslope recharge areas which kept the water levels high near the stream, leading to chemically reducing conditions and the growth of mosses. 50% of the DOC export from the soil occurred during the 10% of the study period with the highest flows. Even during storm events, water is unlikely to travel more than 10 meters to the stream, focussing the search for the immediate origin of DOC export on the riparian soils. It shall also be important, though, to consider the extent to which DOC from upslope contributes to the conditions at the riparian interface between soils and surface waters.

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USE OF AIRBORNE ELECTROMAGNETIC MAPS FOR QUALITATIVE AND QUANTITATIVE ESTIMATION OF SULFIDE CLAYS

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Increased oxidation of sulfide clay (aluna) as a result of rapid isostatic land uplift and deep ditching is causing serious environmental problems in coastal regions of Finland. In the Quark region the quality of waters in streams and river mouths has deteriorated and most spawning-grounds have been seriously damaged. The general regional destribution of sulfide clays has long been known. However, in the evaluation of environmental hazards related to work in specific watercourses, a good knowledge of the location, quality and quantity of sufide clay would is of utmost importance. Reliable estimates on a regional scale would also be essential for areal planning. Present techniques for mapping of sufide clays are based on expensive field work, including sampling and analysis of vertical profiles as well as ground-geophysical surveys.

Research was initaiated in 1989 at the Department of Geology, Åbo Akademi University, to evaluate the usefulness of low-altitude aerogeophysical maps for qualitative and quantitative estimation of sulfide-clay occurrences. Such mapping is being carried out from about 30 m above the ground at 30-50 m intervals along lines spaced some 200 m apart. Slightly more than 50% of Finland has to date been covered with the survey. Because of their relatively high electric conductivity, their surfacial position and their extensiveness in the horizontal plane, clay horizons strongly affect electromagnetic (EM) fields induced above the ground. Therefore, even thin layers of conductive clay cause anomalies in the EM maps. Sulfide clay is identified because its inductive properties are typically such that the ratio between the imaginary EM component (caused by the secondary electromagnitic field) and the real EM component (caused by the primary field) is anomalously high.Several basins, 0.5-1 km^2 in size, with known sulfide-clay occurrence were selected for a pilot study. At a number of sites the clay sequence was sampled at 20-50 cm depth intervals. The samples were measured for their conductivity and chemical composition. The results show a good agreement between the conductivity, the content of metals and the data from the airborne electromagnetic survey. A first arithmetic model for the delineation and characterization of sulfide clay was elaborated. To verify and further develop the model, detailed sampling and chemical analysis will be carried out during June to August, 1991. Results of this work will be presented.

THE LONG-TERM (100 YEARS) ACCUMULATION AND RELEASE OF TOXIC METALS IN ACIDIFIED SOILS UNDER GRASSLAND AND NATURALLY-REGENERATING WOODLAND

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The Classical field experiments at Rothamsted Experimental Station began in 1843. Forty years after this, in 1883, parts of two arable experiments on Broadbalk and Geescroft fields were fenced off and left. We have followed the changes in soil chemistry by analysing stored samples collected periodically over the 100 years since these experiments began. We have compared the changes under these naturally-regenerating woodlands with those under limed and unlimed grassland cut for hay. Earlier papers reported changes in soil pH. This paper reports the next stage in this unique study - that of real long-term changes in soil chemistry arising from atmospheric and other inputs.

Samples were collected from Broadbalk and Geescroft Wilderness and Park Grass on average every 25 years. These were air-dried and stored in sealed glass bottles. We have analysed them for pH, water soluble (1:1 soil:water extract) and exchangeable ions, and water extractable, 'exchangeable' and total Al and heavy metals, with solvent extraction and graphite furnace atomic absorption. Atmospheric deposition has also been measured: data on N, S and Cl are available from the last century, on H^+ and other inorganic ions for at least 20 years, and metals are being monitored at present.

Broadbalk Wilderness contained 3% $CaCO_3$ at the beginning of the study. Its soil pH did not change from 8.0 until the most recent sampling, but all the $CaCO_3$ has been lost. Geescroft Wilderness soil contained no $CaCO_3$ in 1883. Its pH has fallen from 7.1 to 4.1 through inputs of acidity from the atmosphere, mineralization and organic acid release. The pH of unlimed Park Grass soil has fallen from about 5.8 to 5.0 through the same inputs as Geescroft and nutrient removals in the hay.

Changes in soil chemistry are to some extent what would be expected from known inputs from the atmosphere and pH changes. The effect of increasing acidity in the soil of Geescroft Wilderness is seen in decreasing amounts of base cations and CEC, and base cations have moved down the profile. In Broadbalk soil the leaching of Ca can be followed to considerable depth. Sulphate and Cl have been increasing with increasing atmospheric deposition, but most recent data suggest that SO_4-S is now decreasing in surface soil as deposition decreases. Amounts of heavy metals in the soils have increased with time and there is some indication of uptake by the trees and mobilization where soil has become acid.

The data are being used to test the PROFILE and MAGIC models. Soil mineralogy, needed for the PROFILE model, is being studied at the Macaulay Land Use Research Institute. Results will be given in the final paper.

GEOCHEMISTRY AND EVOLUTION OF DEEP SALINE GROUNDWATERS IN THE CENTRAL PART OF THE FENNOSCANDIAN SHIELD

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A country-wide survey on deep groundwater composition and conditions has recently been performed within the Finnish part of the Precambrian crystalline Fennoscandian Shield. The results obtained from some 70 sampling sites, from lithologically varied crystalline rock suites, demonstrate the heterogeneous compositions of groundwaters in the crystalline basement. Groundwater types with bicarbonate, sulphate or chloride as the major anion, and various mixtures of these, have been found. Bicarbonate waters tend to be characterized by low TDS (total dissolved solids) (< 1 g/l); sulphate waters usually have a TDS from 1 to 10 g/l, and the TDS in the chloride waters varies from a couple of grams to values close to 180 g/l. The chlorine data (Fig. 1) show the large variation in salinities (from 1 to 100 000 mg/l), and the typical increase of salinity with depth.

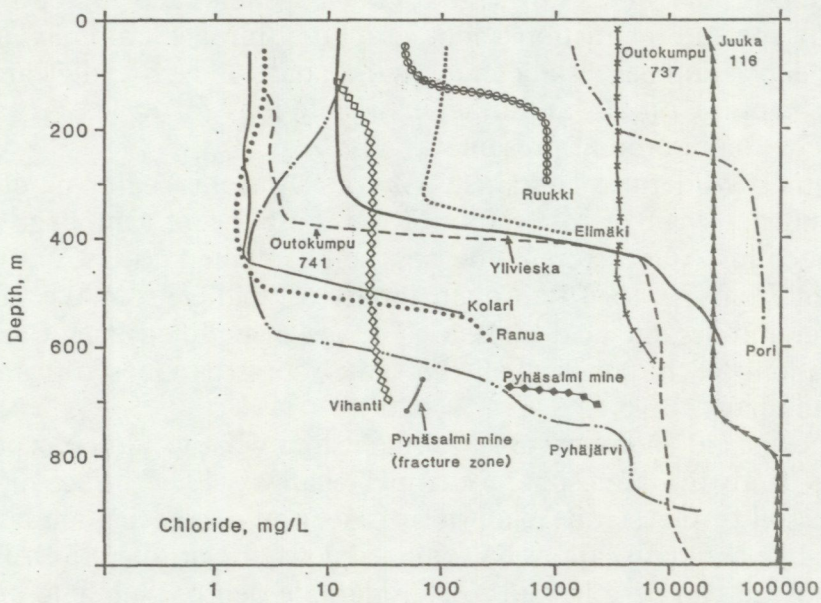


Fig. 1. Chloride values versus depth at various drill hole waters.

Outside coastal areas covered by earlier stages of the Baltic Sea, most of the saline waters have elemental ratios, which distinctly deviate from marine values (Fig. 2), and concentrations that by far may exceed the values in ocean waters. Although the involvement of sea water during some previous stage of the geochemical evolution of the groundwaters cannot be excluded, it is, however, obvious that the waters have been affected by extensive water-roch interaction reactions, which have modified the previous elemental concentrations and ratios, probably under prolonged time scales.

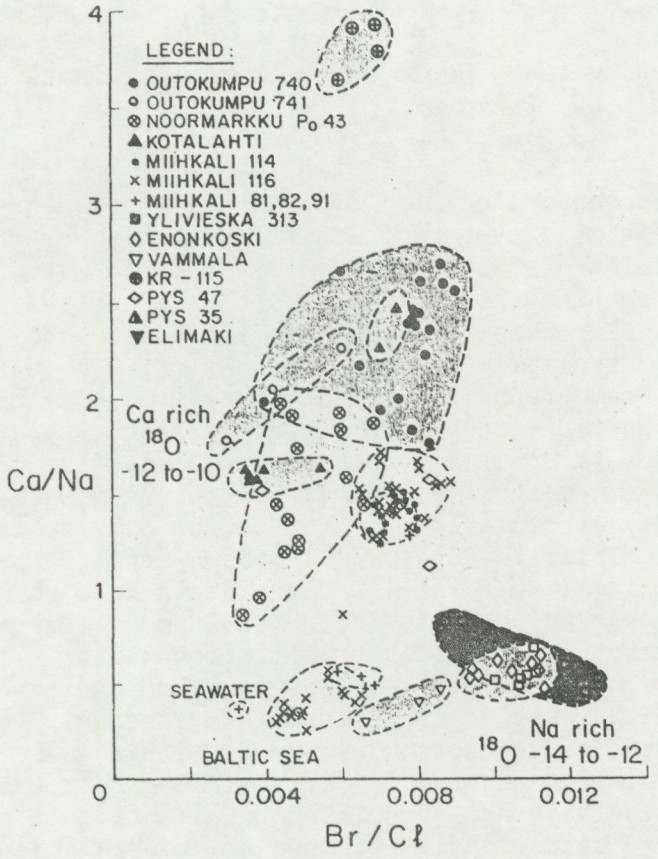


Fig. 2. Ca/Na versus Br/Cl of saline groundwaters and brines in Finland.

The tritium values of the saline waters and brines are usually low and do not indicate recent meteoric waters. The ^{14}C datings of saline waters point to long residence times of several thousand years demonstrating the ancient nature of these waters. Within the $\delta^{2}H$ - $\delta^{18}O$ diagramme the most highly saline waters have isotope values which plot above the meteoric water line. Such exceptional values, only found in highly saline waters and brines, are interpreted to have resulted from the effective fractionationing mechanisms associated with low-temperature water-rock interaction reactions. Various mechanisms for these non-meteoric isotope values have previously been proposed, the essential prerequisites being a closed hydrogeological system, with a low water/rock ratio, and expanded time-scales of up to millions of years. Hence, the results from various isotopic studies seem to confirm the long residence times already suggested by the high salinities of the waters.

As the geochemical and isotopic features of the saline and highly saline waters are indicative of the long residence times and isolated nature of these waters, the rock suites hosting the saline waters could be considered as potential repository environments. More detailed studies in the saline water environment are recommended.

APPLICATION OF SOURCE-ROCK ANALYTICAL METHODS IN THE STUDY OF THE DEGRADATION OF ORGANIC MATTER IN RECENT MARINE SEDIMENTS, AARHUS BAY, DENMARK

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Intensive hydrocarbon exploration over the last few decades, has led to the development of a number of analytical tools for the description and characterization of fossil sedimentary organic matter. These analytical tools are suited for both bulk and detailed characterization of soluble and solid organic matter, and include methods such as Rock-Eval" pyrolysis, Pyrolysis-Gaschromatography (Py-GC), Gaschromatography (GC), Gaschromatography-Mass Spectrometry (GC/MS), thermogravimetry, and various microscopy techniques. The data reported here form part of an attempt to apply a number of these analytical methods to the study of organic matter degradation in recent marginal marine sediments. The study is centered on the "Station 6" site in Aarhus Bay, Jutland, Denmark. This station is well suited for such investigations, because the site is situated at 16m water depth, in a sheltered area, with a high sediment accumulation rate (880 g/m^2yr) and very limited mixing of the bottom sediments (homogenization depth = 2.5cm). The bottom waters are oxic over the entire year, but the oxygen concentration is low, and the benthic macrofauna is accordingly very scarce. Oxygen is exhausted in the bottom sediments within 1-2mm of the surface, and the degradation of organic matter in the bottom sediments is more or less exclusively achieved through the action of sulphate-reducing bacteria. The bottom sediments consist of dark-coloured muds with organic contents in the range 1.4-2.2 wt-% org. C. The sedimentary environment can be assumed to have remained essentially constant over a reasonable timespan, and the overall degradative state of the sedimentary organic matter may thus be assumed to increase with depth. Hence, analyses of samples from a depth profile of the bottom sediments, will yield an indication of the changes in organic matter composition, occurring as a consequence of progressive organic matter degradation. Such analyses reveal a gradual decrease in organic carbon content over the upper 10cm, coinciding with the interval of maximum intensity of sulphate reduction (peak intensity at 6cm). This decrease is paralleled by an increase in total sulphur content, reflecting the formation of sulphide minerals, mainly pyrite, in the bottom sediments, as a consequence of bacterial suphate reduction. Further, changes in pyrolysate composition over the same interval indicate progressive elimination of functional groups from the sedimentary organic matter. Pyrolysate aromaticity, as calculated from Py-GC traces, decreases over the same interval, probably reflecting degradation of fatty acids. In addition, GC analyses of the distribution of normal alkanes in organic extracts also points to the elimination of functional groups from plant epicuticular waxes.

REGIONAL VARIATION OF TL, GA, IN, BE, CR, V, AS, SE, TE AND BI IN DRAINAGE SEDIMENTS

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A suite of lake and stream sediment samples from a variety of geological and geographical settings in Canada were analyzed for the trace elements Tl, Ga, In, Be, Cr, V, As, Se, Te, and Bi. The samples were drawn from the National Geochemical Reconnaisance (NGR) archive, and come from six different areas of Canada. Geochemical data from both the original NGR survey and from the results of reanalysis were entered with geological and other map layers into a Geographical Information System (GIS). The goal is 1) to provide baseline data for these elements in drainage sediments from a variety of settings; and 2) to examine spatial patterns of element variation in relation to geological and other factors.

The archived samples consisted of the -80 mesh size fraction; for reanalysis, samples were ball-milled to -200 mesh and totally dissolved in $HF-HClO_4-HNO_3$. The following summary therefore represents total rather than partial determinations. As and V were also in the original NGR suite of elements; the new determinations yield higher levels for these two elements in some lithologies.

Element	Units	Method	Max.	Min.	Median	N
Tl	ppb	ICP-MS	3220	14	126	741
Ga	ppm	ICP-MS	38.4	0.6	13.2	741
In	ppm	ICP-MS	350	<10	44	741
Be	ppm	ICP-ES	103	<0.2	1.3	741
Cr	ppm	ICP-ES	767	4.4	42.2	741
V	ppm	ICP-ES	560	5	61	741
As	ppm	Hydride-AAS	2070	0.6	6.6	741
Se	ppm	Hydride-AAS	6356	18	446	741
Te	ppb	Hydride-AAS	100	<15	<15	739
Bi	ppb	Hydride-AAS	1982	14	126	741

Preliminary statistical and GIS analysis indicates that: 1) Se content is elevated in lakes as compared to streams, except for lakes at high latitudes; this pattern is positively correlated with Loss-On-Ignition as confirmed by a scatterplot of Se vs. LOI. 2) Maps of V and to a lesser extent Cr show a marked spatial association with the distribution of mafic rocks, particularly evident from one of the sampled areas (N Vancouver Island). 3) Be is particularly high over a granite batholith in New Brunswick, but low over mafic rocks on Vancouver Island. A collage of maps for each element on which the boundaries of generalized geological units are superimposed will be shown on the poster.

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CHEMICAL CHANGES IN SOME SOUTH-WEST SWEDISH PODSOL PROFILES DURING A FIFTY YEARS PERIOD.

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In the thirties and the forties Professor Sante Mattsson and his colleagues at the Agricultural College of Sweden collected a number of soil samples from the southern and middle parts of Sweden. One of their aims was to study the formation of podsol soils in relation to the hydrological conditions. The sampling was predominantly carried out in trenches starting from wetland and going upwards along the slopes of the hills.

In the present study some of the original places are resampled. The sampling sites presented in this lecture are rediscovered within 25 m at Annerstad (West of Ljungby, Småland), and at Unden (North-West of Karlsborg, V. Götland) the distance is 5 m, which is known because the exact site of the original trench is still visible. Besides the published results, I also had the opportunity to interview the now diseased Kaarel Vahtras, who performed the original chemical measurements fifty years ago.

The soil samples are stored at the Agricultural University of Uppsala, and a study is performed with the aim to scrutinize whether or not they are reliable to chemically remeasure after approximately 50 years of storage. The result showed that this can be done during specific conditions. The soil content of humic matter should not be too high, and the treatment and storage of the samples will also influence the reliability.

Because of the outline of the original soil sampling in slopes, it is possible to study the differencies in the chemical changes in relation to moisture. In the resampling the most wet part is excluded, because the present study is only focused on podsol soils.

The impact of acidic load on the mainly fine sandy podsol soils is detected even in the deepest samples (140 cm deep; in the C-horizon). The changes are e.g. lowering of the base saturation, increase of the total acidity and soluble aluminium.

The results show that the acidic impact is higher in the lower (wetter) than the upper (dryer) part of the slope. This is interpreted to be due to the moisture conditions in the soil profile and the relationship to the ground-water level.

EFFECTS OF CLIMATIC CHANGES AND HUMAN IMPACT ON THE ELEMENT TRANSLOCATION WITHIN CLOSED GEOSYSTEMS DURING THE POST-GLACIAL PERIOD (POMERANIA, POLAND)

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In order to determine old processes of washing out various elements from morainic deposits and soils and their accumulation in sedimentary basins, an analysis was made of deposits infilling closed geosystems located on the Vistulian morainic plateaux of Pomerania (NW Poland). The study of the fill deposits embraced:

- the determination of some physical parameters (wet density, water content),
- the analysis of their chemical composition to determine the content of mineral and organic matter, silica, and selected major and trace elements (Na, K, Ca, Mg, Al, Fe, Mn, Cu, Zn, Ni, Pb),
- the radiocarbon dating of selected samples of organic deposits.

In the plateau basins under study with their evapotranspiration type of hydrological regime, the processes significantly contributing to the accumulation of fill deposits were those of chemical and mechanical denudation, taking place here from the end of the Late Glacial through the Holocene till modern times. Given the chemical composition of the fill deposits, their age and sedimantation rate, the stratigraphic differences in the rates of total and selective migration of the particular elements were determined.

It was found that at the close of the Late Glacial and in the Preboreal mechanical denudation was predominant. At the time chemical denudation was restricted primarily to the translocation of amorphous substances, mainly opal, and compounds of aluminium and iron. The leaching of carbonates was negligible; their share in the total amount of substances translocated due to chemical denudation did not exceed a few per cent.

At the close of the Preboreal and the beginning of the Boreal, with the expansion of natural forest vegetation a dramatic, more than 1000-fold decrease in the intensity of total, especially mechanical, denudation took place. It was accompanied by a relative increase in chemical denudation, but its structure changed significantly. There was a marked dominance of carbonate leaching, while metals featuring prominently in the migration series of elements were Cu and Na with Zn and Fe dropping to increasingly farther positions.

During the mesocratic stability of vegetation (the Atlantic) the lowest levels of mechanical and chemical denudation were recorded. In the structure of chemical denudation carbonate leaching still had the largest share, but its absolute intensity was its minimum. This was the time of the dominance of mineral matter recirculation in the phytocenosis, due to which their washout from the soil was restricted to a minimum.

The start of the Subboreal marked a periodic activisation in the migration of lithophilous elements due to changes brought about by the economic activity of the Neolithic man. Generally, this was the time of an increase in the absolute intensity of the leaching of carbonates and such metals as Mg, Na and Cu. In the second half of the Subboreal there was also an increase in the intensity of the selective migration of iron and manganese, which was associated with advancing soil acidification.

With the beginning of the Subatlantic, especially over the last 1000 years, an increase in mechanical denudation can be registered as well as a change in the intensity of migration of a number of elements. The first position in the migration series is now occupied by manganese and, in the last few hundred years, also other heavy metals, with Ca and Na occupying the final positions.

Application of Groundwater Geochemistry to Health Risk Assessments and Land Development Planning In Canada

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Approximately 26% of the Canadian population is dependant on groundwater supplies; dependency varying from 17% in Quebec to 100% in Prince Edward Island. In many regions of Canada surface water utilization has been maximized and in some cases over stressed. Provinces are now turning more and more towards groundwater development to meet their domestic and industrial needs.

Geochemists working in the fields of groundwater hydrogeochemistry and hydrology have a unique opportunity to be actively involved in three main environmental spheres governing the use of groundwaters; namely 1) The establishment of drinking water guidelines and standards, 2) Involvement in environmental health risk assessments, and 3). Groundwater utilization as part of land development planning and landscape ecological analysis.

Examples are given showing how groundwater geochemical data from both regional and detailed sampling surveys in various regions of Canada can be used to a). determine exposure rates to toxic elements in waters, b). assess multiple health risk factors, c). aid in setting of drinking water standards d). outline regions and determine percentage of population where elemenal intakes may be deficient, and d). aid in urban and rural land development where groundwater utilization is required for domestic and industrial purposes.

A close liaison between groundwater geoscientists and officials from all levels of government responsible for urban/rural development and health care is required if costly and sometimes detrimental effects of land and water development are to be avoided.

THE EFFECT OF INJECTOR TINE DESIGN AND SOIL TYPE ON THE SUBSURFACE DISTRIBUTION OF COPPER AND ZINC IN SLUDGE AMENDED SOILS

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Recent European Council legislation (Directive L181, 1986) has prevented the land spreading of untreated sewage sludge, and new Directives are aiming to prevent dumping of sludge in coastal waters and at sea. Many alternatives have been proposed, and subsurface disposal on land (injection) is one of the most viable in terms of minimising cost, nutrient loss and visual, odour and groundwater pollution.

As with any type of land disposal, the volume of sludge that can be injected depends on its heavy metal loadings and the subsequent enrichment of the soil, and specific limits have been set by the EC to control the potential phytotoxic and zootoxic effects of the metals. Both metal lading and environmental impact are influenced by the movement and distribution of metals such as copper and zinc in sludge amended soil. As a result, a series of experiments have been devised to examine the behaviour of Cu and Zn after injection, and the factors that affect these patterns. Sludge was injected into two different soil types using three tine designs. Soils were analyzed for Cu and Zn and characterised in terms of pH, organic carbon, particle size, cation exchange capacity and Fe and Mn contents.

Results show that each type of tine creates distinctive soil disturbance patterns, which can be ranked in terms of area affected as winged tine > paraplow > straight tine. this is regardless of soil type. Sewage sludge is pumped into the voids created by the passage of the tine, so it follows that sludge distribution is greatest in the case of the winged tine and least with the straight tine.Most of the Cu and Zn present in sewage sludge is associated with solid fractions and their distribution closely reflects those of the sludge and the loosening created by the tine. The winged tine disrupts the entire area between the blades (600mm) and creates a relatively even distribution of metals, which, in addition, appear to move out of the zone of influence. Metal concentrations are therefore only slightly elevated with respect to background concentrations. the main effect of the straight tine is restricted to within about 120mm of the tine slot, although this is somewhat dependent on soil type. Metal concentrations therefore consist of two distinct populations, with maximum concentrations up to 8 and 11 times the background concentration for Zn and Cu respectively. This relationship is soil type dependent, but is also extremely variable within soil types. It

is suggested that this variability is largely the result of differential performances of the injection equipment, rather than intrinsic differences within the soil.

From this work, it can be concluded that:

1) Each tine creates distinctive patterns of soil disturbance, which vary as much within as between soils.

2) The pattern of soil disturbance is reflected by metal distribution.

3) Soil factors and metal type have only a secondary influence on distribution.

LONG-TERM CHANGES IN THE CHEMISTRY OF INLET AND OUTLET STREAMS IN THE MIRROR LAKE WATERSHED.

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The Mirror Lake watershed has been the focus of a long-term study initiated in 1965 to investigate lake-watershed interactions. This research is part of a broader program studying biogeochemical processes in the Hubbard Brook Valley of New Hampshire. Chemical data (pH, cations, anions and nutrients) were collected from 3 inlet streams and at the lake outlet during 23 years. Long-term trends in stream chemistry were analyzed to detect responses to changing land-use patterns within the watershed and to assess the effects of changes in precipitation chemistry in the northeastern region of the United States.

The most conspicuous effect of localized human activity has been an increase in stream Na^+ and Cl^- concentrations as a result of road salt applications during winter. A major roadway was constructed through the NE subcatchment of the watershed during 1969-1971. Increasing salt concentrations in the NE tributary became apparent in 1975 and have continued to increase at an average annual rate of 90 ueq $Cl^-L^{-1}year^{-1}$. The NE tributary contributes approximately 10% of the total inputs to the lake's water budget. Increasing salt concentrations in the lake outlet were not evident until 1978 but have risen continuously since that time. By 1989, Cl^- concentrations in the outlet had increased by 196%.

Precipitation chemistry has been monitored at the Hubbard Brook Experimental Forest since 1963. Reductions in SO_2 and NO_x emissions in the eastern United States have resulted in a 28% decrease in SO_4^{2-} deposition and an 18% decrease in H^+ concentration in precipitation since 1975. During the same period, outlet SO_4^{2-} concentrations decreased by 21% and inlet concentrations decreased by 9, 10 and 16%. Decreases in SO_4^{2-} in the 3 inlet streams were comparable to the 12% decrease in the drainage stream for watershed #6 located in the Hubbard Brook Experimental Forest. Reductions in SO_4^{2-} were accompanied by a decrease in base cation concentrations in 2 of the 3 inlet streams. Changes in base cations at the NE inlet could not be evaluated due to the influence of elevated Na^+ concentrations associated with road salt. At the NW and W inlets, the decrease in base cations (24 and 36 ueq/L) was comparable to the decrease observed at watershed #6 (31 ueq/L). Base cation concentrations were higher in the inlet streams relative to watershed #6, therefore, their relative change over time (11 and 16% decrease) was smaller in comparison with the drainage stream at watershed #6 (26%). Decreases in SO_4^{2-} were comparable to decreases in base cations and therefore no significant changes in H^+ concentrations were evident in the tributaries or the lake outlet.

CANCER MORBIDITY IN RELATION TO DRAINAGE GEOCHEMISTRY IN NORWAY

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The Cancer Registry of Norway collects cancer epidemiological data. A nationwide atlas of municipal incidence rates of 25 types of cancer during 1970 - 79 has been published. The Geological Survey of Norway collects geochemical data characterizing the environment. Nationwide geochemical maps of the contents of up to 31 elements in widely spaced samples of drainage sediments are available.

These two data sets, the one being epidemiological and the other geochemical, constitute the basis for investigations of geomedical relationships in Norway. Average values for cancer incidence rates and contents of chemical elements have been tabulated for each of 193 geographical units constituting either large municipalities or aggregates of small neighbouring municipalities. Each unit has a population between 10.000 and 50.000. Various statistical methods were applied in the search for possible covariations between the two data sets.

Principal Component Analysis was used to describe the data sets. Calibration models for prediction of cancer incidence rates based upon chemical data were built using Partial Least Squares and Principal Component Regression. These multivariate methods seem to be unfeasible, apparently due to lack of data for the most dominating causes of cancer and because levels for the ratios of signal to noise are low.

Pair-wise correlation analysis was applied in two ways (a) within subsets obtained by dividing the bulk of all municipalities and municipality aggregates into subgroups (N=15-52) according to degree of urbanization, location, climate etc. or (b) by comparing only data from the two members of each of 81 selected pairs of neighbouring, uniform municipalities or municipality aggregates.

The bivariate methods produce numerous high correlation coefficients. However, for various reasons (e.g. the great number of coefficients involved), the significance of these coefficients cannot be estimated. Some of the disclosed high correlation coefficients may, nevertheless, be of interest because (i) the obtained number of correlation coefficients apparently significant at a certain level of confidence is 2-3 times greater than the number that can be expected from correlations between sets of random figures and (ii) both methods (a) and (b) in some cases produce high correlation coefficients for the same type of cancer versus the same element. Examples of such correlations are (1) "Skin cancer other than malignant melanoma", which repeatedly shows good correlation with a number of elements, the coefficients being negative for e.g. K, Ca, Na, Sr and Cr and positive for Ce, La and Pb, (2) cancer of the male kidney, which is positively correlated with Sr and (3) cancer of the female breast which shows positive correlation versus Ce and La.

Aspects of this type of geomedical comparison will be discussed, emphasis being put on the fact that the study is empirical. No conclusions about causes or effects can, therefore, be drawn. However, this type of work may eventually lead to causual hypotheses for later testing with other methods.

Heavy metal contamination in sediments expressed by the gradient method

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When elevated heavy metal concentrations in sediments are only due to a corresponding elevation of the organic matter content the gradient method according to Cato (1977) can facilitate interpretation. The method is based and tested on fine-grained coastal, clastic, surface sediment of similar age and sampled with an even distribution within an area, independent of the exact grain-size distribution. Consequently one is not only refered to samples from pronounced deposition areas. The gradient (inclination coefficient) of the relationship between the metal in question and the organic carbon content is measured using regression analysis. The gradient represents the metal load independent of the variation of the organic matter concentration in the sediments. The steeper gradient, the higher the level of heavy metal contamination, i.e. the more polluted is the sediment. Examples are given from areas along the Swedish west coast of gradients and temporal changes in gradients caused by changes in municipal- and industrial discharges .

MAPPING, MONITORING AND MODELLING HEAVY METAL WASTE FROM A CENTURY OF MINING AND SMELTING IN THE COEUR D'ALENE DISTRICT, IDAHO, NORTHWESTERN USA

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Over a century of base metal, especially silver, mining and smelting in the Coeur d'Alene River Valley, in northern Idaho, NW USA, has caused heavy metal pollution over an area of of at least 1000 square kilometers. Until tailings ponds were established in 1968, wastes were allowed to enter the river, which flooded annually or semiannually, carrying contaminated water and sediments over the flood plain and depositing them on flats and in lakes, as well as in Coeur d'Alene Lake, the local base level of the Coeur d'Alene River. Geochemical analyses and modelling in the Smelterville Flats area (a flood plain near the smelter) and in Killarney Lake (a flood plain lake) have shown extremely high concentrations of heavy metals, as well as low pH values that are buffered in the unsaturated zone on the flats by carbonate gangue minerals. Trenches were dug to water table on the flood plain in order to obtain stratigraphic sections at all the sampling sites. In the Selterville Flats area, Pb concentrations range up to 120,000 ppm, Zn to 90,000 ppm, Cd to 1000 ppm, As to 370 ppm, Ag to 160 ppm, and Sb to 150 ppm, at depths ranging up to 3meters. Metal speciation studies have shown that >99% Ag, >90% As, >90% Sb, and >50% Zn reside in residual (mainly sulphide) phases, and are not mobile under existing pH conditions. However, only about 25% Cd and 15% Pb reside in residual species. An average 40% Pb, 30% Zn, and 15% Pb reside in oxide species, and approximately 15% Pb and 5% Cd in the easily exchangeable sites on clay minerals. 50% Cd, 10% Zn, and 5% Pb reside in organic species, and could be released under oxidizing conditions. Specially adapted freezer boxes and freezer probes were used to extract undisturbed stratigraphic sections of lake bottom sediments as well as lake bottom water samples from the flood plain lakes, known locally as lateral lakes. In Killarney Lake the highest metal concentrations were discovered at 40 to 50 cm sediment depth, being covered by slightly less contaminated sediments deposited since the tailings ponds were established. The highest concentrations recorded to date in Killarney Lake are 40,000 ppm Pb, 30,000 ppm Zn, 150 ppm Cd, 380 ppm As, and 40 ppm Ag. Geochemical modelling shows that organic comlexing of some heavy metals is causing release into the biosphere. Death of many local wetland species has been attributed to Pb poisoning. Preliminary studies on the other nine lateral lakes of the Coeur d'Alene River indicate similar or worse conditions.

THE HYDROTHERMAL TRANSFORMATION OF THE OPALINUS SHALE, SWITZERLAND ; FORMATION OF SMECTITE AND ZEOLITE MINERALS

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Shales, due to their high sorption properties, and low permeabilities are being considered as suitable rocks for low and high level radioactive waste repositories. Very little experimental data exists on the effects of the interaction of the waste form and the host shales (such as changes in temperature and solution composition). The presence of concrete barriers could significantly alter the in-situ pH, solution composition, and mineralogy of the shales. Possible mineralogical changes include: quartz and calcite dissolution and precipitation, the alteration of clay minerals, and the formation of zeolite minerals. The formation of clay (especially smectite) and zeolite minerals is quite important when assessing the waste storage potential of shales. To investigate these possibilities experiments were conducted using the Opalinus clay formation (middle Jurassic) in Mont Terri, Northern Switzerland.

Batch experiments were run in small volume teflon bottles (7 ml, perfluoralkoxy) which were loaded with charges and then placed within 50 ml titanium hydrothermal reactor vessels (2 per vessel). These reactors were sealed, and placed onto a rotisserie unit inside an oven set at 175°C for reaction times of up to 17 days. Individual reactors were removed at specific intervals, quenched in cold water, and opened. The solution pH was measured at 25°C using a Ross combination pH electrode, and the solids were separated from the solutions. Each reactor was charged with 0.14 grams of the 80-200 mesh size fraction of Opalinus clay, and 7 ml of solution of varying composition (NaOH, KOH, and $CaOH_2$). The solids were characterized and analyzed by x-ray diffraction. Mineral composition of the starting shale as determined by x-ray diffraction is: 40% quartz, 20% kaolinite, 15% muscovite/illite, 15% calcite, 5% chlorite, 3% mixed layer smectite/illite, 2% siderite and trace pyrite.

The table below gives quench pH and reaction products versus time data for 0.1m NaOH, 0.1m KOH, and 0.005m $CaOH_2$ solutions. Solid phase transformations as determined by x-ray diffraction in experimental runs after 17 days include the disappearance of kaolinite and the formation of clays and zeolite phases in the 0.1 m NaOH and 0.1 m KOH experiment. There was no detectable change in the mineral composition of the 0.005m $CaOH_2$ solution. The precipitation of these clay and zeolite minerals will greatly enhance the sorption capabilities of the Opalinus shale.

Time, Days	quench pH, 25°C	Reaction Products
	0.1m NaOH solution	
0.00	12.73	* * * * *
3.00	12.13, 12.17	analcime, smectite
10.01	11.37	analcime, smectite, mica/smectite
17.04	11.23, 11.29	analcime, smectite, mica/smectite
	0.1m KOH solution	
0.00	12.73	* * * * *
10.01	11.90	kspar, phillipsite
17.04	11.55, 11.56	kspar, mica/smectite
	0.005m $CaOH_2$ solution	
0.00	11.78	* * * * *
3.00	7.64,7.65	none
10.01	7.57	none
17.04	7.35, 7.50	none

* * * * * starting solution before solids added

Effects of Acid Load on Leaching Forest Soil Columns Amended with Lime and Phosphorus: II. Phosphorous Chemistry

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ABSTRACT

Research has suggested that acid load on forest soils has a negative impact on P supply. The use of lime combined with calcium phosphate in reducing soil sensitivity to acidic deposition was suggested. In this study a laboratory leaching experiment was conducted to investigate the effectiveness of $CaCO_3$ and $Ca(H_2PO_4).H_2O$ separately and in combination on altering phosphorus chemistry in forest soil columns leached with distilled water (DW), H_2SO_4 (S) and HNO_3 (N) in two differing molar ratios with H_2SO_4 (S1:N1 and S1:N2). Soil columns were packed with weakly podsolized silt loam from south Sweden and leached continuously with DW and S, S1N1 and S1N2 at pH 3.7 to an equivalent of two years' rainfall during an 8 month period of leaching. Apart from control (C) three chemical amendments were mixed into the top 5 mm of the mor humus; $CaCO_3$ at 5 t ha^{-1} (L), $Ca(H_2PO_4).H_2O$ at 332 Kg ha^{-1} (P) and L and P combined (LP).

Transported phosphorus (Bray2 extract) in the control columns accumulated in the upper level of the B horizon; however, acid leaching significantly lowered extractable P compared to DW leaching. Soil pH-H_2O in the amendment free (control) columns was not significantly affected by any of the four leaching solutions. In the presence of amendments, phosphorus transport was significantly influenced by the differing dissolution of the amendments in the acids. For example, significant levels of Bray2 extractable phosphorus were found in the A and upper B horizons in L and LP amended columns. This new zone of P accumulation could be attributed to increased dissolution of Ca and of HCO_3 from $CaCO_3$ which precipitated P as calcium phosphate.

We conclude that transport and distribution of P was influenced by acid input and mainly controlled by chemical amendments. Therefore we shall discuss the use of chemical amendments as mitigating agents to acid impact on forest soils.

NITRATE TRANSPORT IN SUBALPINE STREAMS LAKE TAHOE BASIN, CALIFORNIA-NEVADA

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Over 3100 samples were collected and analyzed for nitrate-N during a period of 8 years in up to 7 streams in the basin of Lake Tahoe, California-Nevada. Nitrogen is at times the limiting nutrient in this large (156 km^3) ultra-oligotrophic lake, which has been gaining in productivity and loosing clarity since the early 1960's due to anthropogenic nutrient inputs. This paper reports on efforts to develop a linear model to relate nitrate-N concentration to two discharge variables and to fit the model to the data using linear regression. The goal was to compare the relative contribution to nitrate-N load of two dominant water types: "short flow-path water" that dominates during storms and snowmelt, and "long flow-path water" that dominates base flow. The first variable in the model is $1/(1+KQ)$, where Q is discharge and K is a constant. This variable is derived from a mixing model for two water types in an open system. The second variable uses either cumulative water discharge or cumulative nitrate-N load for the water year.

The data were grouped according to flow regime, with fall, winter and snowmelt runoff (Phase I) as one data set, and snowmelt recession and summer low-flow (Phase II) as a second data set. Step-wise linear regression was used to find the best value for K and to examine the contribution of the second independent variable given the first. For the Phase I data, both independent variables made a highly significant contribution to explaining the concentration variance in six of the seven watersheds tested. R^2 values ranged from 0.22 to 0.45. In four of the catchments, the coefficient for $1/(1+KQ)$ was negative; this is consistent with a precipitation source for nitrate-nitrogen, with a pulse of nitrate released during early snowmelt. In three of the catchments, the coefficient was positive; in two of these, there is a likely anthropogenic source for nitrate, and in the third, nitrogen fixation by alder may provide a source of nitrate in base flow. For the phase II data, the coefficient for $1/(1+KQ)$ was zero in three catchments, and positive in four, reflecting both biological uptake and baseflow enrichment. For one catchment, the model was fit to data for eight separate water years; it explained between 18 and 80 percent of the variance in nitrate-N concentration. The results of this study indicate that the model can be used to distinguish anthropogenic nitrate sources from background, and to develop predictive models for estimating total load.

The Effect of Heavy Metal Pollution on Soil and Biont

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Abstract

This paper presents: soil, biont and human health in Shuikoushan Industrial District for the history of the last hundred years has been systematically investigated. Made an analysis of 200 and more soil samples and 50 and more biological samples and made a study of 60 cases human cell genetics, it is indicated that : heavy metal content in the soil of the industrial district is evident greater than the regional background level. With heavy metals in vegetable and rice of the industrial district are greater than the control plot, the frequency of the sister chromatid exchanges (SCE) of the peripheral blood lymph cell and the rate of chromosomal aberation of the workers and staff are greater. The research results showed that : soil polluted by heavy metals in the industrial district have had certain effect to biont.

DYNAMICS OF NONEXCHANGEABLE CALCIUM, MAGNESIUM AND POTASSIUM RELEASE FROM PODZOLIC SOILS IN SOUTHERN QUEBEC, CANADA

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Terrestrial ecosystems underlain by igneous and metamorphic bedrock are considered to be among the most sensitive to acidification because the weathering rate of the minerals is not rapid enough to neutralize all incoming acidity and to release sufficient amounts of nutrient cations (Ca, Mg and K) to the soil solution and exchange complex. As such, soil mineral reactions with ambient solution are critical processes of the overall response of soil and vegetation to the atmospheric deposition of dilute inorganic acids. However, it has been demonstrated that mineral weathering rates determined in the laboratory generally exceed mass balance field estimates by two to three orders of magnitude. Moreover, despite the abundant literature concerning the weathering of pure minerals in laboratory experiments, very few reports exist on the weathering kinetics of untreated soil minerals (no Fe and Al coating removal). The objectives of this study are i) to quantify the temporal dynamics of calcium, magnesium and potassium release to solution from two podzolic soils as a function of solution pH, ii) to compare the relative efficiency of organic and inorganic acids (citric vs sulfuric) in promoting cation release and iii) to examine the influence of coating removal.

A laboratory experiment was conducted with the Bhf and C horizons of both soils profiles using a miscible displacement technique. Prior to the experiment, the soil exchange complex was Sr-saturated (four washings with 0.1 M $SrCl_2$ at a 1:10 soil to solution ratio) to eliminate the possible contribution of the exchangeable phase to Ca, Mg and K release. Moreover, rock samples taken from the C horizons of both profiles were grounded to compare nutrient cation release from fresh uncoated minerals and naturally coated minerals having the same particle size. Duplicate 1 g samples of < 2-mm soil materials were loaded into a 25 mm diameter Nuclepore filtration assembly containing a 0.4 µm polycarbonate membrane attached to a fraction collector and a peristaltic pump. The materials were leached at a flow rate of 0.05 mL min^{-1} with citric or sulfuric acid solutions having a pH of 3.0, 3.7 or 4.5 for up to 1080 hours in the presence of toluene. The ionic strength of all leaching solutions was controlled using 0.01 M $SrCl_2$. Calcium, Mg and K concentration in solution were determined by AAS.

The results indicate the following trends: i) for any given horizon, cation release increases with solution acidity; ii) at a given pH value, cation release to solution proceeds at a much faster rate with citric acid solutions; iii) for a given profile, release rates are higher for the C than for the B horizon and iv) Ca, Mg and K transfer to solution is at least one order of magnitude faster for the fresh uncoated minerals as compared to naturally coated minerals.

GEOCHEMICAL EXPLORATION FOR TRACE ELEMENTS IN THE LATIUM REGION. ARSENIC, MERCURY, GOLD AND TIN IN STREAM SEDIMENTS AS PATHFINDER ELEMENTS IN ASSESSING ENVIRONMENTAL PULLUTION

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Summary

RIMIN S. p. A. carried out, in the period 1989-90, geochemical prospecting surveys in the Latium Region (Central Italy) aimed at assessing the mining perspectives of Quaternary alkali potassic volcanic formations widespread outcropping in this Regions, as regards base metals, Rare Earths and Au, on the basis of stream sediment analisys.

This exploration project has been carried out on behalf of the Italian Ministry of Industry and in cooperation with the Dept. of Earth Sciences of Rome University. All the major constituents and approx. 20 trace elements were analysed in the course of different campaigns of exploration. More than 3000 stream sediment samples were collected and analysed in the reconnaissance campaign and more than 1000 in the more detailed surveys aimed at individuating the origin of the anomalies pointed out by the results of the preliminary exploration.

Among the elements examined, Au, As, Sn and Hg seem to be the most interesting because the study of their distribution constitutes a logical link between geochemical exploration and environmental geochemistry; distribution of these elements is therefore presented and discussed here.

Arsenic pattern seems to indicate mainly a natural origin, in the sense that its distribution indicates the aureoles in the vicinity of idrothermal deposits.

Mercury was analysed only during the second stage of exploration. Its anomalies are frequently originated by human activity and sometimes indicate mineralization of Hg and of other elements for which Hg play the role of pathfinder element.

Tin distribution points out precisely solid waste dumps and secondarily high backgrond level of peculiar geochemical provinces.

Gold distribution seems to be twofold interesting. Sometimes Au anomalies indicate high background levels and/or dispersion aureols; more frequently Au anomalies pointed out heavily polluted areas, where, moreover, no Au mineralizations can be found due to the geochemical and geological feature.

AIRBORNE GAMMA-RAY SPECTROMETRY: A MULTI-PURPOSE METHOD FOR ENVIRONMENTAL MAPPING.

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The use of airborne gamma-ray spectrometry (AGRS) for quantitative surveys has been well established since the 1970s. Applications have included the mapping of the natural radiation environment, the distribution of fall-out products from accidents such as Chernobyl, and the geochemical mapping of the surface abundance of K, U and Th. Data have been used by health physicists, geochemists and geologists. Recently AGRS has been the first step in the identification of areas where there may be a radon hazard. Airborne gamma-ray spectrometry is thus an essential tool for mapping important aspects of the natural geochemical environment and is a component of the International Geochemical Mapping project.

The purpose of this paper is to draw attention to the possibility of another important application for AGRS relating to the geochemical mapping of large areas. Conventional surface geochemical surveys are commonly based upon different sample media in different geographic regions, for example glacial till, lake sediments, stream sediments, soils, laterites, desert wash. Even in a region where a single sample media has been used, there can be difficulties in normalizing abundance levels where the work has been carried out over a period of time, or by different organizations. Problems of this type clearly increase as areas of coverage are expanded. They constitute one of the major obstacles to the compilation of a coherent global geochemical atlas.

AGRS measurements can provide continuous profiles over all types of terrain. Consistent mean surface abundances can be obtained because there are standardized calibration and data reduction procedures, established through the International Atomic Energy Agency. The 3 elements determined are important geochemical indicators. Potassium is a major element, U and Th are mobile and immobile trace elements respectively. If K, U and Th abundances from both AGRS and conventional surface sampling are available along common profiles, it is possible to normalize data obtained from diverse surface sample media in terms of the AGRS measurements. Normalization indices can be determined for each block of conventional surface data. Studies are being undertaken of the correlation which exists between these two sources of data in different environments, and also of the validity of extrapolating the normalization indices derived in this way to other major and trace elements. If these extrapolations can be justified there will be an additional important benefit from using AGRS as a standard technique in global geochemical mapping.

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ENVIRONMENTAL GEOCHEMISTRY AND GLOBAL GEOCHEMICAL MAPPING

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Eighty-six chemical elements occur in the solid state in the natural surface environment. At the present time approximately half of these are known to have some biological effects, and there is no reason to suppose that this list is complete. Life has evolved (and is evolving) in this environment and it is possible that, collectively, most elements have some significance to life. It is desirable therefore to have as complete knowledge as possible of the geochemistry of surface materials, to document the background distribution of elements around the world in order to recognize abnormalities caused by human intervention or natural events.

Earth scientists are familiar with the fact that the world contains interlinked geological and geophysical features at all scales, from global, through continental and regional, to the microscopic. Geochemical parameters are known much less completely, especially at the coarser (national and continental) scales. Nevertheless, there is evidence that large geochemical features exist and more will be found as data are acquired. In order to understand any phenomenon, and in order to recognize to problems, it is often advantageous to obtain a general overview of the relevant parameters before selecting specific features for detailed examination. Environmental geochemistry is no exception.

Unlike geology and some geophysical parameters, there are geochemical maps for less than 20% of the earth's surface. Of equal or greater concern is the fact that not more than 4 elements are common to the principal data sets! It is only in the last few years that consideration has been given to adding many elements of environmental interest to analytical suites. Until recently almost all systematic mapping programs have been dominated by mineral exploration considerations. From a practical viewpoint there are strong arguments for conducting comprehensive systematic surveys as rapidly as possible. There are examples in a number of countries of regulatory bodies setting arbitrary "safe limits" on toxic elements in the environment, in ignorance of the natural range of values, or neglecting consideration of complicating factors. There is an urgent need for systematic geochemical base-line data which can serve a dual economic-environmental purpose. This double function is particularly important to developing countries.

An International Geochemical Mapping project was launched in 1988 under the auspices of UNESCO/IUGS to establish the framework upon which systematic base-line data can be obtained. One eventual product will be a World Geochemical Atlas. A report will be given concerning the present status of the project.

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MAPPING ANTHROPOGENIC CHANGES IN THE INORGANIC GEOCHEMISTRY OF URBAN DRAINAGE SYSTEMS USING ORGANIC LAKE SEDIMENTS.

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Lake sediments and waters were collected from the main urban region of Newfoundland, Canada, to map the nature and extent of geochemical variations due to urban development. Lake sediment was chosen as the main sample medium because lakes provide an efficient way of sampling the drainage network and are widely distributed throughout the area. Moreover, geochemical background data from lake sediment are available for the whole of Newfoundland, permitting a comparison of abundance levels within the urban region as a whole with other geologically similar but less disturbed areas.

Sediment and water samples were collected from 60 sites from all lakes in the urban core and most of the lakes within a surrounding area of 320 km^2. After pH determination, the waters were passed through a 0.45 micron filter, acidified with 1 mL of HNO3 prior to chemical analysis. The dried lake sediments (<0.18 mm fraction) were analysed for 41 elements (total content): As, Au, Br, Ce, Co, Cs, Eu, Hf, La, Mo, Na, Rb, Sb, Sc, Se, Sm, Tb, Th, U, W, Yb and Zn by INAA, and Al, Ba, Be, Bi, Ca, Cr, Dy, K, Li, Fe, Mg, Mn, Nb, P, V, Sr, Ti, Y and Zr by a combination of ICP-OES and AAS. In addition acid-soluble levels of Ag, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb and Zn were determined by AAS, and organic carbon content was estimated from loss on ignition at 500°C.

In the study area as a whole levels of Pb, Zn, Ag, Mo, La, Ce, Eu, Sm, Tb, and Yb are significantly higher ($p<0.0001$), and LOI and Br significantly lower than the surrounding less disturbed area of similar Hadrynian volcanic and sedimentary rocks. Within the study area the main anthropogenic effects are the high levels of Pb, Zn, Ag, Mo, Cr, V, Cu, Ba, Al, Hf, Cu, Au, W, Mg, U, K, Sb and Bi in lakes from the urban core of the City of St. John's itself, which contain the highest Pb levels encountered on the Avalon Peninsula, accompanied by elevated levels of an unusual geochemical association that may be typical of multi-source urban pollution. Elevated levels of Cd, Zn, Ni, P and Ag are found in the southwestern part of the area around the site of a former steel mill, with the highest values occurring in sample sites adjacent to roads.

These results suggest that although urbanization has modified the natural geochemical environment in the St. John's urban area, the changes have been fairly modest and localized. Even in the area of strongest pollution the drainage systems maintain a viable population of trout and arctic char, although periodic fish kills do occur. The results provide an overview of the geochemical environment in 1990 on which more detailed and focussed studies can be based, and will be useful in planning any future environmental monitoring program.

PIG SLURRY MINERALIZATION AND N_2O-PRODUCTION

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Farming systems in North-Western Europe are characterized by high application rates of animal manure. Both NH_3-volatilization and denitrification are enhanced under these conditions depending on the actual modes of application and environmental conditions. In a laboratory experiment with soils amended with slurry, NH_3-volatilization, C,N-mineralization and N_2O production, as a result of both denitrification and nitrification, were measured.
After 14 days of an aerobic incubation at 25°C, 65 percent of the organic carbon contained in a single pig slurry dressing on a loamy soil mineralizes. As such, even at low application rates, 5 ton per ha or 26.9 g pig slurry kg^{-1} dry soil, conditions are favourable for denitrification and for N_2O-production :

1° Pig slurry contains a large amount of easily decomposable organic matter, i.e. 92 % (Van Soest, 1963). Both soil borne organisms and the ones present in the slurry flourish on this substrate, thereby depleting O_2 present in soil pores and producing NO_3^- in a first phase.
2° Anaerobiosis is enhanced due to the large amount of water, i.e. 96 %, added with each dressing.
3° Finally, NO_3^- present in anaerobic sites is serving as electron acceptor, leading to N_2O and N_2 production.

However, N_2O can also be formed during nitrification (Bremner & Blackmer, 1978). Therefore, gaseous losses of nitrogen due to denitrification [N_2O, N_2] were measured from acetylene treated soil samples and losses due to nitrification from didin, as a nitrification inhibitor, treated samples. The nitrogen lost due to denitrification [N_2O+N_2] was 28.7 mg-N kg^{-1} dry soil and N_2/N_2O was 4.3. The N_2O-production due to nitrification was 8.5 mg-N kg^{-1}. A small amount of NH_3, 1 mg NH_3-N kg^{-1} D.S., evolved from the control soil and less than 5 mg NH_3-N kg^{-1} D.S., i.e. 4 % of the total nitrogen content of the pig slurry, from the amended soil.

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PODZOLISATION IN FINNISH LAPLAND

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This study is being carried out as part of the Lapland Forest .Decline Project, the aim of which is to determine the effects of industrial emissions from the Kola Peninsula on the fertility, and acidification status and susceptibility of forest soils in Finnish Lapland.

The aim of the study was to determine the vertical distribution of different elements down the soil profile, and then to use a range of extractants to determine the forms in which these elements are distributed in the different horizons of podzolic soils. This information is to be used in assessing the susceptibility of podzolic soils to accelerating soil acidification, and to gain a deeper understanding of podzolic processes.

The soil samples were taken from the 14 ion-balance monitoring plots established on gradient lines running through Lapland from the two major point emission sources in the Kola Peninsula (Nikel/Zapoljarnyi and Montsegorsk). The plots are all located on dry sites with a topsoil of sorted fine sand. The tree stands consist of Scots pine, with a varying admixture of fell birch. Soil samples were taken down to a depth of ca. 45 cm at four points around the circular sample plots. The different horizons were measured and detailed descriptions made. The cores (diam. 5 cm) were cut carefully into 1 cm-thick sections. The following analyses were carried out on the fresh samples: pH(H_2O), total analysis (dry ignition/2N HCl extraction), complexed Fe and Al (pyrophosphate), free Al and Fe oxides (dithionite), exchangeable cations (NH_4OAc, pH 4.65) and free cations (0.01N NaCl).

The result shave been used to determine the distribution of base cations into reserve/immobilized, exchangeable and free forms. These parameters are essential in elucidating the mechanisms involved in soil buffering based on cation exchange. The results also provide information about the reserves of easily weatherable material in the uppermost mineral soil layers. The distribution of Al, Fe, Mn, Si and organic matter and pH conditions at the interface between the E and B horizons in the mineral soil also provides the data needed in gaining a deeper understanding of podzolisation processes.

THE EFFECT OF TEMPORAL AND SPATIAL VARIABILITY ON SOLUTE TRANSPORT IN FIELD SOILS

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Solute movement in the unsaturated zone is controlled by different physical, chemical, and biological processes. Furthermore the spatial heterogeneity in natural fields may have a significant effect on field scale solute transport. Thus, when modelling solute movement in heterogeneous soils there is generally a need to couple the hydraulic and (bio)chemical processes with the spatial variability in hydraulic and chemical parameters. The complexity of the problem, however, nescessitates different simplifying assumptions. Thus, although water flow close to the soil surface is in general highly transient, many investigators of field scale solute transport in the unsaturated zone use the simplifying assumption of steady-state flow. In addition, experimental studies of transport processes in soils are often conducted under steady-state flow conditions. Because the steady-state flow assumption is common and may simplify the transport problem considerably, it is of interest to investigate the effect of temporal hydrological variability on solute transport in different soil types under climatic, soil and vegetal conditions prevailing in the field.

The effect of temporal hydrological variability is illustrated here by a comparison between solute arrival times predicted by a transient and a steady-state flow model. Data for four different soil profiles with detailed measurements of their hydraulic properties and their variation with depth are considered. Daily measurements of meteorological data are used as input parameters in the transient simulations that include snow and frost dynamics, interception of precipitation, and evapotranspiration. The results indicate that the steady-state flow model may provide estimates of the mean solute advection that are compatible to those based on the transient flow model [1].

The effect of spatial variability in hydraulic and chemical parameters on the field scale mass flux of reactive solute through the unsaturated zone is illustrated here using a stochastic framework. The source of solute is assumed to be distributed at the soil surface of a heterogeneous field. The considered reactions are equilibrium and nonequilibrium sorption-desorption, and first order loss of solute. Different correlation properties between the hydraulic and chemical parameters are investigated. The results indicate that spatial variability in the reaction rate coefficients may have a significant effect on the field scale mass arrival of solute at a given depth, e.g. the groundwater table, [2,3]. In addition, the stochastic framework is used for assessing the uncertainty in predictions of field scale solute transport that is related to the size of the solute source and the sampling area [4].

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ABSTRACT

THE GEOCHEMISTRY OF ENDEMIC GOITRE - EXAMPLE FROM SRI LANKA*

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Recent research has shown that etiology of endemic goitre is multifactorial while the chief causative factor is iodine deficiency in the diet. The prevalence of goitre is extremely high in certain parts of Sri Lanka, with Horana in the Western Province having 44% and Angunawela - Daulagala in the Central Province having an incidence of 38-40%.

A geochemical survey carried out in the Angunawela-Daulagala area showed that 90% of the water wells had less than 100 ppb of iodine with the mean value being 54 ppb. The mean values for the other chemical parameters were : F^- 297 ppb; Cl^- 35 ppm. NO_3 9 ppm; Na^+ 511 ppm; K^+ 7 ppm; Ca^{2+} 22 ppm; Mg^{2+} 6 ppm; Fe 1.2 ppm; Mn^{2+} 53 ppb. The mean iodine content of the soils of the study area was 2 ppm as compared to 9 ppm in the Wariyapola area known to be a non-goitre region situated in the dry zone of Sri Lanka.

All hydrogeochemical data of the study area were classified using cluster analysis. It was observed that there are four main clusters, one of which coincided with the area with the highest incidence of endemic goitre. This cluster had very low values for the chemical parameters Cl^-, NO_3^-, alkali metals, alkali earths, Fe and Mn when compared with the other clusters.

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*Contribution of the Environmental Geochemistry Research Group (EGRG)

HEALTH RISK EVALUATION OF CERTAIN COMPOUNDS FOUND IN CONTAMINATED SOIL.

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Persistent contaminants in soil represents an environmental health hazard that has to be considered when former industrial sites are being abandoned or redeveloped. As part of a redevelopment plan, the Institute of Environmental Medicine has been asked to evaluate the health risks associated with exposure to certain compounds contaminating soil at a former gas work site and a wood preservation plant.

The routes of exposure considered in the health risk assessment were inhalation of vapour and soil dust, ingestion of soil and dermal contact. Small children were considered the primary risk group. The soil exposure estimates (Table 1) were adopted from a Danish report (1).

Table 1. Estimated daily exposure to soil (g).

		Inhalation	Oral	Dermal
Children,				
3/4-4 years old	mean		0.2	1
	max	0.01	3	10
	pica		max 10	
Adults	mean		0.025	0.1
	max	0.03	0.1	1

The soil at the gas work site was heavily polluted with coal tar containing polycyclic aromatic hydrocarbons (PAH). In addition, phenols, cyanides, sulfur compounds and heavy metals were found.

The critical health effect associated with exposure to PAH in coal tar is cancer, in this particular case skin cancer through dermal contact with PAH in soil. Ingestion of phenols, cyanides and sulphur compounds may cause acute health effects. Recommended guide-line values for these contaminants were generally obtained by dividing the lowest observed effect levels with appropriate safety factors.

The metals considered, arsenic, cadmium, lead and mercury, may cause both acute and chronic health effects. The average dietary intake of toxic metals may approach the provisional tolerable weekly intake levels (PTWI) set by FAO/WHO. In our risk assessment, the guide-line values for cadmium and mercury in soil were set based on a maximum

intake through ingestion of soil corresponding to 10 % of the PTWI-value for a child. For arsenic, the guide-line value corresponds to 5 % of the PTWI-value for a child. The suggested guide-line level for lead may increase the blood-lead level in a child by a few µg/l, at the most.

At the wood preservation plant, the soil was contaminated with copper, chromium and arsenic. The highest arsenic concentration found was 38 000 µg/g soil. Based on the acute health effects of arsenic upon repeated exposure, a maximum daily ingestion of 10 g of soil for a 10 kg child and an uncertainty factor of 10, a guide-line value of 10 µg As/g soil was suggested for soil in a residential area.

Our guide-line values for selected contaminants in soil are summarized in Table 2.

Table 2. Guide-line values for contaminants in soil (µg/g).

Coal tar:	6-10	**Arsenic:**	10
PAH:	10	**Mercury:**	2
Benzo(a)pyrene:	0.1	**Cadmium:**	10
Phenol:	100	**Lead:**	30
Free cyanide:	10		

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MODELLING OF NITRATE LEACHING FROM AGRICULTURAL SOILS ON A REGIONAL SCALE IN THE NETHERLANDS

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KEYWORDS:
Manure Excess, N-fertilizer, Nitrogen Balance, Legal Regulations, Empirical Nitrate Model, Geographic Information System.

ABSTRACT:
A method of regional modelling and mapping of nitrate leaching from agricultural soils is presented. In 1991 this method was used to assess effects of legal regulatory measures with respect to application of manure on agricultural soil in The Netherlands. Nitrate leaching was calculated with an empirical model, based on field experiments and survey. The model was implemented in a geographical information system, containing maps of manuring rates, soil type, land use and depth of the groundwater table. Four scenario's have been examined in which production of nitrogen and phosphate in animal manure, application time of animal manure, maximum phosphate load from animal manure, ammonia emission rate from stables and spreading of manure were varied.

INTRODUCTION:

The rate of production and applicability of animal manure in The Netherlands are not balanced on a regional scale. In the south-east part of the country annual production of nitrogen and phosphate in animal manure exceeds annual crop withdrawal two, resp. three times. Also N fertilizer application on grassland is very high. To make it even worse the south-east part of the country consists of sandy soils, where groundwater is very vulnerable to nitrate pollution.

FIELD EXPERIMENTS:

In the period 1986 - 1988 a field survey and several field and laboratory experiments were carried out by the Laboratory of Soil and Groundwater Research of the RIVM to study occurrence and behaviour of nitrate in agricultural soils and in groundwater. Boumans (1989) found an average nitrate concentration under intensively used well drained grassland on sandy soil of 54 mg/l (as N). He also found a clear relationship between nitrate concentration in upper groundwater and the depth of the water table.

EMPIRICAL MODEL FOR NITRATE LEACHING:

Researchers, like Kolenbrander (1981), Vetter et al. (1985), Walther (1989), Steenvoorden (1985) published results of field experiments showing definite, non linear proportional relationships between the N fertilization and nitrate concentration in the leachate of sandy soils. This kind of relationships have been used to derive and calibrate a model for nitrate leaching as a function of soil use, soil type, depth of the water table and application rates of animal manure, dung from grazing cattle and N fertilizer.

APPLICATION OF THE MODEL:
The model was implemented in a geographical information system in order to assess effects of legal regulatory measures proposed to decrease nitrate concentration in upper groundwater.
Input data for the model such as rates of animal manure applications and N fertilizer was provided by the Research Institute of Agricultural Economics LEI (Luesink and Van Veen, 1989). The model calculated nitrate leaching rates of 700 municipalities, (max.) 7 soil types and (max.) 6 types of agricultural land use. The next step was to combine calculated nitrate leaching with an overlay of maps of municipality, soil type, land use and depth of the groundwatertable. Results of these operations are maps of the calculated nitrate concentration of upper groundwater in The Netherlands.

RESULTS:
Results of this study will be discussed in the paper. Some prelimary conclusions are:

- Nitrate pollution of upper groundwater is a wide spread feature in The Netherlands. Nitrate concentrations in upper groundwater exceed drinking water standard (50 mg/l) in about 37% of all agricultural land and over 70% of the sandy part of the country. This will not improve significantly after all measures have been effected.

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INFLUENCE OF COPPER SMELTER EMISSION ON CHANGES OF SOME SOIL PROPERTIES

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The aim of the investigations was to compare some chemical, physico-chemical and physical properties of heavily polluted soils (I-st zone) with those of soils similar morphologically, situated at a considerable distance from the emission centre (II-nd zone) in the region of copper smelter.

Among the pollution indices investigated in A_1 horizon of soils of the I-st zone the highest amounts of copper and than zinc and sulfur accumulated. Heavy pollution leads to a distinct soil degradation, which manifests itself in unfavourable changes of the soil profile morphology and of physical, physico-chemical and chemical properties of soil profiles, particularly of their accumulation horizons.

The polluted soils chracterize less amount of microaggregates and pores of biogenic character, which proves a reduction of their biological activity. Structural aggregates show a lower waterproof coefficient in contaminated soils what is a reason greater water erosion. Heavy pollution results in unfavourable quantitative and qualitative changes of humus compounds, while fulvic acids show higher percentage in the total organic matter in relation to non-polluted soils. Heavily polluted soils show a higher hydrolitic acidity and less basic cations as compared with non-polluted soils, what manifests itself in a lower sorption complex saturation with metallic cations. The dense vegetation cover of soil and agronomic measures applied in crop cultivation ofen have an unfavourable effect of pollution on changes of soil properties. Therefore the polluted soils, with regard to economic considerations ought to be comprised a special measures even irrespective of economic calculation, to improve the structure forming ability, the organic matter transformation trends and physico-chemical properties of the soils.

THE CONCENTRATIONS OF AS, CO, CR, CU, GA, MN, NI, AND SE IN SURFACE SOILS OF POLAND

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The purpose of the research was to establish baseline concentrations of As, Co, Cr, Cu, Ga, Mn, Ni and Se in the surface soils of Poland. The sampling programme was designed to obtain data representative (ca. 130 samples) of arable soils in Poland, under typical management. Locations directly affected by pollution (point source pollution, roads with heavy traffic, etc.) were avoided. Concentrations of Co, Cr, Cu, Ga, Mn, Ni were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry, whereas As and Se by Hydride-Atomic Absorption Spectrometry.

Since frequency distributions of the all element contents of the soils were positively skewed, the data were transformed to logarithms (base 10) and central tendency and variation were expressed as geometric means (GM) and geometric deviations (GD), respectively.

Mean concentrations of the elements (in mg/kg, dry weight) in the soil samples studied were: As 2.6; Co 3.6; Cr 16.8; Cu 6.3; Ga 4.8; Mn 304.3; Ni 7.4 and Se 0.10. The element contents of the soils correlated very well with amounts of particles <0.002 and <0.02mm diameter ($r = 0.65-0.94$), and with concentrations of Al and Fe ($r = 0.69-0.96$), which indicate that the occurrence of the elements in the soils is controlled mainly by pedogenic factors. The concentrations of As and Cu showed also good correlation with soil organic matter ($r = 0.60-0.61$). All the elements studied had significantly ($P<0.05$) higher concentrations in silty and loamy soils, considered as one group, than in sandy soils. Schematic maps showing regional differences in element contents of soils are presented.

THE USE OF A LITHOGEOCHEMICAL DATABASE FOR EPIDEMIOLOGICAL STUDIES IN CENTRAL SASKATCHEWAN, CANADA

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Studies have indicated that the high incidence of multiple sclerosis among residents of the Canadian Prairies may be partially related to trace elements in soils and ground waters. Since soils are derived from rocks, and ground waters derive their chemical composition from the rocks and soils, a low cost multi-element regional study of bedrock geochemistry was initiated to provide a database for further epidemiological studies.

Over the past 50 years many oil exploration holes have been drilled in Saskatchewan. Rock chips from these holes have been carefully documented (with regard to stratigraphic position), catalogued and archived. Samples of these rock chips were collected from all 96 wells that have been drilled within a 100,000 sq. km area of central Saskatchewan. Much of this area is rural, and residents grow many of their own crops and derive their water from untreated wells. Consequently much of their trace element intake is locally derived. Included in the study area is the community of Henribourg, where there is an unusually high incidence of childhood homes of multiple sclerosis patients.

A total of 720 samples were collected from the 96 wells. With the aid of geophysical well logs the stratigraphic position of each sample was recorded, and all samples were examined by microscope to obtain a brief and systematic description of their lithology, grain size, colour, and other noteworthy features. Subsequently, each sample was analyzed by a) instrumental neutron activation (INAA), and b) inductively coupled plasma emission spectrometry (ICP-AES) following an aqua regia digestion. These techniques provided data for 71 elements and yielded approximately 50,000 analytical determinations. Data for some of these elements were obtained by both analytical techniques, such that the total number of different elements determined was approximately 50.

A preliminary assessment of the data shows that the Henribourg 'cluster focus' for multiple sclerosis is near the subcrop of a metalliferous dark carbonate-rich shale known as the White Specks Formation. Geological maps show that this site is also close to a major structural flexure which could give rise to fracturing of the substrate. Furthermore, this is an area of formation water discharge which could facilitate leakage of metals to the surface. The occurrence of health problems at a site where there is a coincidence of anomalous geological, geochemical, and hydrological conditions is an observation that warrants investigation.

Low density geochemical mapping provides a cost-effective assessment of the environmental geochemistry of broad tracts of land. Indications are that geochemical baseline data of the type obtained for this study may be of considerable value for epidemiological studies.

FATE OF COPPER IN A TROPICAL RIVER SYSTEM AFFECTED BY MINING ACTIVITIES (FLY RIVER, PAPUA NEW GUINEA)

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Abstract

The Fly river in Papua New Guinea has a catchment area of about 76.000 km^2. The sediment transport has been estimated at 74 million tons per year. In the headwaters of the Fly river a copper is located which discharges about 80.000 tons of copper containing tailings in the river system. Concentrations of copper in the tailings vary but are about 800 µg/g. Further downstream causes a dilution of the copper content by sediments from tributaries. The most important one being the Strickland river which contributes about two third of the total sediment load entering the Fly estuary. A geochemical model was constructed of the river based on laboratory adsorption studies and validated by extensive field date (a four years time series is now available on the water and sediment chemistry). The dissolved copper contents are less than 5 µg/l due to the relatively high pH of the river system. Mineralogical analysis of the sediments and suspended matter showed the presence of calciumcarbonate which buffers the pH of the system.

The copper contents of the sediments in the estuary are still close to natural conditions despite the fact that the mine has been in operation for several years. An oceanographic survey of the estuary was conducted in 1990 and found extensive areas with fluid mud at the bottom of the estuary. Calculations showed that the mixing of the uncontaminated fluid mud layers with the contaminated river sediments entering the estuary is responsible for the present low levels of copper in the estuary.

Laboratory investigations on the mobility of copper on contaminated fluvial sediments showed that part of the copper is amenable to release in the estuarine environment. Detailed studies on the kinetics of this process are underway.

Apart from these geochemical studies a biological study has been carried out to determine the toxicity of copper in the tailings and sediments under laboratory conditions. Field surveys were carried out to determine the correlations between increased sediments load and increased copper levels on the diversity and biomass of the fish population in the Fly river.

NATURAL AND MAN-MADE GEOCHEMICAL PATTERNS IN FENNOSCANDIA FROM ULTRA-LOW DENSITY SAMPLING

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The ultimate object of Global Geochemical Sampling (GGS) under IGCP 259, International Geochemical Mapping, is to collect large composite samples of different materials at 3000-5000 stations over the whole globe. In a first phase GGS is carrying out pilot sampling in different global environments in order to work out procedures for the future global sampling. A pilot project in Fennoscandia is going on at the Åbo Akademi University. The aim of the project is to collect bulk composite samples of stream water, overbank stream sediment, humus (A horizon) and till (C horizon) from 49 drainage areas 500-5000 km^2 in size.

Water is being sampled from the mouth of each drainage area 12 times during one year and one overbank sediment sample has been collected from the surface and another from depth (40-80 cm) at the same sites. Till and humus are being sampled from 20 sites within each drainage area. This far we have got chemical analyses of one water sample from each area, of all overbank sediment samples and of the till samples from Finland.

Like till (composite samples for each area), the water and overbank sediment should both reflect the geochemistry of the whole drainage area as they are sampled at the mouth of the drainages. The critical value of the correlation coefficient (r) for the 95% level of significance is 0.28 (n=49). For the correlation water-sediment r is >0.28 (0.34-0.70) for Al, Ca, K, Mg and Na whereas it is <0.18 for Ba, Fe and Mn. Element contents in till (n=15, critical value 0.51) do not correlate at all with contents in water (r=0.47 for K and <0.26 for the other elements) and not with contents in sediment (r<0.11, 0.24 for Al).

The preliminary results so far indicate that till, stream water and overbank sediment even at this very low sampling density and with so few samples show regional anomaly patterns clearly related to known large-scale geological features. This shows that the method is useful for the global sampling program.

The influence of ore provinces and anthropogenic activity on the composition of the sediment and water samples is also indicated. Till reflects bedrock geology and mineralized provinces well, but is not yet anthropogenically affected. The surface samples of the overbank sediment are slightly polluted in some places, while the bottom samples are mostly pristine. Both waste water (e.g. from mines) and airborne pollutants (e.g. Pb in areas with a heavy traffic) are indicated. E.g. the upper sediment sample from Kvina in SW Norway has 260 ppm Mo, while the lower sample has only 15 ppm Mo. The big Knaben Mo-mine is situated 35 km upstreams. At other sites, where mining activities have ceased the sediment shows decreasing metal contents towards the surface. At many sites Al is distinctly lower at the surface than at depth. This is thought to reflect leaching in the surficial parts due to acid rain.

The results of the project may be used to estimate the present and potential future input of elements from different drainage areas to the seas. The water from the rivers draining the sulphide-rich clays and tills on both sides of the Gulf of Bothnia, but especially on the Finnish side, are enriched in at least Al, Fe, Cu, Pb and Co. Ditching and land uplift lowers the water table and cause enhanced leaching of metals from the clays and the till.

HYDROGEOCHEMICAL SURVEYS FOR ENVIRONMENTAL ASSESSMENT

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P. SHAND, P.L. SMEDLEY, and R. FLAVIN

Shallow groundwaters (wells, springs and river baseflow) provide a three-dimensional sampling of the near surface environment providing information on baseline geochemical conditions and on the impact of man. Results from two areas of the UK with contrasting land use - Northern Ireland and south-west England - are used to illustrate the use of surveys and hydrogeochemical maps.

Groundwater baseflow to rivers and streams has been sampled in two 400 km^2 areas of Northern Ireland (Sperrin Mountains and Mourne Mountains) at a density of about one sample per km^2. These two regions, situated mainly on Pre-Cambrian metasediments and Tertiary granites respectively, include areas where relatively pristine natural conditions prevail against which the extent of various types of pollution (acid rain, agricultural activities, forestry, mining and local industry, etc) may be identified against the natural baseline resulting from mainly geological processes. Chemical analyses of some 26 elements or parameters from each site have been used to create synoptic maps which can be used as the basis for environmental assessment of each region.

The combination of pH, alkalinity, aluminium and calcium maps can be used to assess the areas most vulnerable to acidification. The Mourne Mountains is a particularly sensitive area where aluminium usually exceeds 200 $\mu g\ l^{-1}$ Al_T; at high flows the pH is likely to be lower and aluminium concentrations in excess of this value would be inevitable. The low calcium (<2 mg l^{-1}) in baseflow over much of the Mourne Mountains indicates an area of risk to fish stocks. The bedrock geology and drift cover of the Sperrin Mountains gives rise to groundwater baseflow which provides greater buffering of surface waters than in the Mourne Mountains, except in a few isolated regions.

The impact of agricultural activities on water quality has been determined using NO_3, P and the K/Na ratio. These three parameters help to identify areas of disturbance of the land above the likely natural conditions and show where areas of intensive farming, e.g. silage slurry, high fertiliser applications, are to be found. Whilst the areas where the impact of agriculture is greatest can be clearly identified, the quality of baseflow seldom indicates pollution as high as in other parts of the UK; nitrate concentrations rarely exceed 2 mg l^{-1} (NO_3-N).

The concentrations of a number of essential or toxic elements (Al, Cu, Be, La, Si, Fe, Mn, Ba, Sr, Li, Y, B, Cd, Zn, F) are also shown and anomalies can be identified which relate to geological background, mining activities or to the low pH of the baseflow.

In south-west England intensive dairy farming has had a noticeable impact on the shallow groundwater quality. Nevertheless, the underlying hydrogeochemistry may be related to changes in the geology of the Carboniferous sediments. Additional criteria (TOC, NH_4) have been used to assess the impact of pollution.

BERYLLIUM IN RIVER BASEFLOW, SHALLOW GROUNDWATERS AND MAJOR AQUIFERS IN THE UNITED KINGDOM

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Beryllium is potentially a highly toxic element which may be mobilised under acidic conditions in natural waters. In this paper the occurrence of beryllium and controls on Be solubility are examined using a range of data sets from the UK. Regional hydrogeochemical surveys have been conducted for a variety of objectives in various parts of western Britain where shallow groundwater is important for local public and domestic supplies and as a contribution to river baseflow and reservoirs. Beryllium occurrence in wells, springs and streams is considered in relation to pH, geology and in conjunction with other elements with which it may be geochemically associated, particularly in the formation of complex ions that may affect solubility. The highest concentrations of beryllium (≥ 5 $\mu g\ l^{-1}$) are associated with stream baseflow draining Tertiary granitic rocks of the Mourne Mountains.

A survey of trace elements in groundwater from the principal aquifers in the UK has also provided a database on the occurrence of beryllium. In carbonate aquifers, beryllium is not present above the detection limit of 0.05 $\mu g\ l^{-1}$. Concentrations may rise to around 1 $\mu g\ l^{-1}$ in certain non-carbonate lithologies where the pH is below 6.5 The occurrence of beryllium where detectable, is described in relation to the hydrogeology of each area and the geochemistry of other elements.

Interstitial water profiles from the unsaturated zones of the Lower Greensand (Surrey) and Triassic Sandstone (West Midlands) show that beryllium is mobilised during weathering within the top 10 m of each aquifer. Concentrations in excess of 10 $\mu g\ l^{-1}$ may occur in the Triassic sandstones and concentrations in excess of 1 $\mu g\ l^{-1}$ may persist to the water table.

In this paper the likely controls on beryllium mobility in surface and groundwater are discussed based on field evidence and geochemical modelling. Environmental implications and the problems for water resources management are considered for the UK in particular with reference also to other countries.

LEACHABILITY OF ORGANIC CHEMICALS

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Chemical leaching is the major pathway for ground water contamination. The measurement or prediction of organic chemical leachability in subsurface environments is, therefore, of significant concern and controversy. The ability to forecast leachability, as well as chemical transformation, is fundamental to exposure analysis and risk assessment activities. The partition coefficient or retardation factor is used as an indication of the leachability of compounds and is the parameter most often measured in the laboratory with static (batch) or dynamic (column) techniques. The objective of this paper is to review the two measurement techniques for various classes of organic chemicals (polar, non-polar, and ionogenic) and to discuss the potential problems in interpreting laboratory data.

Several considerations when conducting static measurements are: volatility of contaminant, soil to solution ratio, competitive sorption, equilibration time (kinetics), biological inhibition, and presence of immiscible or miscible phase. Volatilization losses of the compound into the headspace could cause overestimation of the partitioning to the soil phase or could be incorrectly accounted for by biological or chemical transformations. Partitioning of non-polar organic compounds is not significantly affected by soil to solution ratio, although partitioning of polar and ionogenic compounds is affected. Partitioning of polar and ionogenic compounds is also affected by ion exchange with the sorbent surfaces. Because hydrophobic partitioning is the major mechanism of sorption of non-polar organics, these compounds do not exhibit competitive sorption. The polar and ionogenic compounds are influenced by the ionic strength of the solution and other ions competing for the exchange sites.

Equilibrium kinetics can be studied by batch techniques where the significance of the size of the soil aggregates and the amount and type of organic carbon present are examined. Removal of parent compounds due to biological transformations can also cause an overestimation of the soil to water partition coefficient. Presence of anthropogenic sources of organic carbon, such as free or residual phase fuel hydrocarbon, can complicate the measurement of the partition coefficient.

Column studies are used to make dynamic measurement of the partition coefficients and require similar considerations as batch measurements. Examples of compound breakthrough curves from column experiments and methods to evaluate this data for forecasting exposure are presented. Comparisons are made between static and dynamic measurements of partition coefficients.

MIA/MIR (Multivariate Image Analysis/Multivariate Image Regression) - tools for geochemical remote sensing, monitoring, modelling and mapping.

by

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Abstract

MIA (Multivariate Image Analysis) and MIR (Multivariate Image Regression) extends the well-known data analytical tools PCA and PLS-regression into the image regimen. Geological and geochemical remote sensing images can be analysed in their proper *problem-dependent* context using MIA/MIR allowing both unsupervised image segmentation/classification (MIA) - i.e. also when *NO* ground truth is available, and for regression (MIR) - when *some* ground truth is present. - It is also possible to implement *contextural* features into both MIA and MIR when necessary.

The general principles behind MIA/MIR is presented and examples from various remote sensing platforms (LANDSAT Thematic Mapper; GEOSCAN; AVIRIS; SAR) will be illustrated. MIA/MIR offers versatile tools for geological and geochemical modelling, monitoring and mapping.

MIA/MIR can also be applied to *compound* imagery, f. ex. combinations of remotely sensed images and various ground-based, e.g. geochemical maps or to ground-based images (maps) alone, e.g. regressions between geophysical, geological and geochemical maps etc.

GEOCHEMICAL ENVIRONMENTAL ZONALITY OF THE LOESSIC HYPERGENIC ZONE IN THE PAMPEAN GEOSYSTEM, ARGENTINE.

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The loessic hypergenic zone and the geochemical processes involved, in respose to the climatic conditions at the present interglacial period, was studied. The balance of radiation (R) and radiation-aridity index (R/Lr) concepts, proposed by Kriger and Petrov, was applied and typomorphic associations for loess, were established. A high correspondence between the SW-NE climatic gradient that characterizes the southeastern plains of South America, and the distribution of landscapes, hypergenic conditions and typomorphic mineral associations, was found applying the geochemical gradient proposed by Fortescue, Strakov, and others.

By means of the R and R/Lr index, six typomorphic associations was stablished for the pampa: a)$NaCl$-$NaSO_4$-$CaSO_4$-$MgSO_4$-$MgCl_2$, b)$CaCO_3$-illite-smectite-$CaSO_4$-Na_2SO_4, c) $CaCO_3$-illite-smectite-SiO_2-$CaSO_4$, d)illite-smectite-$CaCO_3$-SiO_2-Fe_2O_3, e)Fe_2O_3-SiO_2-$CaCO_3$, f)Fe_2O_3-SiO_2. The distribution of these zones shows a definite NW-SE gradient. In the weathering moderate conditions of the pampean steppes, the hypergenic processes intensity increases from SW to NE. This conditions also confirms the genetic twin disponibility-climate as the principal reason of the geochemical and mineralogical inmaturity of the loessic sediments.

Four geoenvironmental aptitude zone for the pampean loessic sediments were defined: 1) deserts and semi-deserts, southwestern of the 25 cm isoyete. Formation of loessic sediments isn't possible. Pedogenetic $CaCO_3$ and lixiviation are scarce. Deflation of silt occurs. R/Lr index > 3.4; 2) semiarid steppe. Formation of loessic sediment and high stability for it. $CaCO_3$ is accumulate in the soil section. R/Lr index: 3.4-1.21; 3) humid steppe. Feeble instability for the loessic sediments. $CaCO_3$ and gypsum tends to be lixiviated. The SiO_2 mobility is weak to moderate. R/Lr index: 1.2-0.88; 4) tropical forest. High instability for the loessic sediment. Isn't forms and, if this exist, it rapidly degrades. Fe_2O_3 and SiO_2 tend to concentrate, and $CaCO_3$ to lixiviate, from the hypergenic zone.

The distribution of the pampean loessic sediments calculated by means of environmental parameters shows a high correspondence with the actual distribution. To the northeastern of the region wide outcrops of loessic sediments are under high degradation conditions. That distribution is on disagreement whith regard to the present environmental conditions. Furthermore, it is stated that the stepparies conditions of stability and formation of the loessic sediments long range, at past, to the argentinian mesopotamia, Uruguay and south of Brazil.

THE GRADIENT OF WEATHERING CONDITIONS IN THE PAMPEAN GEOENVIRONMENTAL SYSTEM.

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In this paper the argentine pampean region was studied, comprehending it as a dynamic and particular geoenvironmental system, with complex structure and history and definible in energetic terms. The weathering conditions in this system shows geographic zonality with a SW-NE gradient, as have been determined. The gradient was established by applying a diagram modification of Strakov and his conceptual model about the weathering crust development.

As is predicted by that model the geochemical mobility of weathering crust components and the intensity of weathering processes increases from SW to NE. The clay mineralogy in soils and loessic sediments and the relation of abundance of the clay minerals are also consistent. The weathering crust of the pampean loessic sediments is of sialitic saturated or hidromicaceus type, with alteration of the primary silicates by hydration and hydrolysis and weak migration of the silica. The geographic distribution of the rains, temperatures, evapotranspiration, climate, natural vegetation and soils, also show a zonality SW-NE.

The predominant superficial winds-directions is also SW-NE. S and SW cold and dry winds blow from the pacific subtropical anticyclone. N and NE wet and warm winds blow from the atlantic subtropical anticyclone. At the present predominate these last, and they are the cause of most rains. Nevertheless, evidence exists that the predominant winds during the last pleniglacial were from SSW and SW. According to the proposed geochemical gradient, the illite, smectite and caolinite neoformation during the loessic singenesis in the present geoenvironmental conditions of the pampean steppes is established. The zonal geographic distribution, according to the SW-NE direction, is assuming as a consecuence of the atmospheric circulation, of the southeastern hemisphere.

In the climatic zonation three limits are to bring out: the desertic belt; the desert-steppe limit; and the steppe-wet subtropical zone limit. That limits have a desplacement along the SW-NE gradient axis on correspondance with the subtropical pacific and atlantic anticyclone dynamic.

According to evidences given by several autors, that atmospheric circulation system would be running from the late Pleistocene, and yet from the times of Quechua diastrofism of the andean orogeny (late Miocene).

THE ENVIRONMENTAL GEOCHEMISTRY OF THE LOESSIC VOLCANIC GLASS AND THE GEOGRAPHIC DISTRIBUTION OF THE PHREATIC WATER CONTAMINATION WITH As, Se, U AND Sb.

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The environmental geochemistry of the loessic volcanic glass and the origin and distribution of the natural contamination of phreatic waters with As, Se, U and Sb, has been studied.

The volcanic glass is, second to the plagioclases, the most important component of the ligth mineral fraction in the pampean loessic sediments. Glass volcanic powder plus illite and smectites (both with low cristallinity) are the main types of clay particles. The glass has ryolitic or dacitic composition. It is enriched in SiO_2, As, Se, Mo and Sb, and impoverished in FeO tot., CaO, MgO, Na_2O, K_2O, Al_2O_3 and MnO, with regard to the upper crust. Se and As present the highest enrichment. The same primary relation of abundance As>U>Se>Sb and anomalous contents of these oligoelements, in the "pure" glass shards, the glass shards with clay, the clay separated of the shards, the all sediment, the associates phreatic waters and the contemporaneous volcanic ash of Quizapú volcano were found .

Moreover, in the all sediment, the glass shards with clay, and the volcanic ash to the Quipazú, has been shown the same absolute abundance of As, Se, U and Sb.

By means of radiation balance, the radiation-aridity index and the compositional gradient SW-NE of hypergenic zone (Kriger, Strakov, Fortescue), the regional conditions for the silice weathering was stimated and the area of potential contamination of phreatic waters, was delimitated. It coincides with the area of the highest environmental stability for the pampean loessic sediments. The weathering crust is in an initial state of its evolution and shows an hydromicaceous section with weak to moderate hypergenic conditions. The weathering process of the loessic volcanic glass is the disolution. The devitrificacion is negligible. The geochemical mobility of the silice is weak to moderate and increases from SW to NE. The volcanic glass disolution is consistent with the measured environmental conditions in the loessic sediments and in the phreatic waters.

Applying the aqueous migration coefficient, the geochemical mobility of silice is maxima for the bicarbonated facies of the phreatic waters, with dissolved solids under 1,100 mg/L.

The loessic volcanic glass is high enriched in all contaminants and constitute the primary source of these oligoelements. By regard to the phreatic water, this enrichment range for As between 2 and 200 times, for U from 10 to 500 times, for Se from 5 to 2000 times, and for Sb between 20 to 500 times.

MOBILITY OF MERCURY IN AQUATIC ENVIRONMENTAL OF PANTANAL, BRAZIL: II. FIXATION MECHANISMS

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The present work was developed in Pantanal, municipality of Poconé, Mato Grosso state, Brazil. The rudimental gold mining activity (garimpo) exists in this area since 18th century, and can be divided in three different cycles of exploration. The latter lasts from 1980 to today.

The great interest for mercury geochemical speciation in sediments arose from the necessity of understanding the transport and fixation mechanisms of the refered metal in the aquatic systems of the Pantanal in order to evaluate the impacts of the mining activities over this environment, once it is necessary to give answers, through cientific works, to great pressure that is being exercised by Governmental Agencies and National and International Environmental Preservation Entities in view of the great importance of the Pantanal ecosystems.

The studies were realized using bottom sediments that were divided in two groups: a) Organics, corresponding to the natural sediments of the Pantanal Formation (recent geologic unit); b) Ironigenous, corresponding to the anthropogenic rejects of the gold exploration activity (garimpo).

Each sample was separated in five granulometric fractions (0,50-0,25;0,25-0,0062;0,0062-0,002mm). Total contents of Hg was determined in all fractions to know the Hg mass balance of that samples.

The clay fraction was chosen for geochemical speciation studies.

The development of sequential selective extraction was necessary to permit the identification and quantification of Hg associated to the main phases constituints of the sediments. The main phases are:

I. Adsorbed on to clay minerals;

II. Organic matter and metalic mercury;

III. Oxides/hydroxides of iron and manganese;

IV. Residual.

Situations of elevated contaminations of sediments with ionic mercury ($HgCl_2$) was simulated in laboratory for the two types of sediments, when studies about the cinetic of absortion of Hg were made.

The results show that there was natural regulation mechanisms on the fixation of mercury by sediments, where it was essentialy associate with oxides/hydroxides of iron and manganese and organic matter.

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ENVIRONMENTAL GEOCHEMISTRY ASPECTS OF ROCHA'S MINE, BRAZIL.

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The area of this work is Rocha's Mine on medium Ribeira Valley, Paraná state, Brazil. This is a lead mine where the metacalcareous rocks aged about 500 millions years old contents lead ore deposits.

The main mineralogical paragenesis has gallene, sphallerite, calcopirite and pirite.

We collected sistematics samples of stream sediments, surfacial waters and scalp hairs of inhabitants of the area. The main objectives were to understand the transport and fixation mechanisms of lead, cooper and zinc in aquatic systems and detect the possibles contaminations of inhabitants by the refered metals.

For stream sediments, besides the total amounts we made selective sequential extrations, where were identified and quantified the associations of the reported heavy metals with the different constituints of the sediments. The main phases were:

I. Adsorbed on to clay minerals;
II. Carbonates;
III. Oxides/hydroxides of iron and manganese;
IV. Organic matter;
V. Residual.

The surfacial waters were analized for total contents of lead, cooper and zinc and the following physico-chemical parameters:pH, Eh, turbidity, total alcalinity, carbonates, bicarbonates, free CO_2, total hardness, consumed oxigen in acidic medium, nitrates, nitrites, ammoniacal nitrogen, organic nitrogen, soluble silica, fluorides, chlorides, sulphates, calcium, magnesium, potassium , total iron and solids in suspension.

Scalp hair samples of inhabitants from Amazonas region and Pantanal (Mato Grosso state) were analysed and considered as references of uncontamined areas and was compared with the results of analogue samples from the Rocha's Mine (contaminated area).

The results show that iron and manganese oxides/hydroxides and organic matter are the main agents responsible for the transportation and fixation of the reported heavy metals in the aquatic systems studied. The results of scalp hair analysis show that incorporation of the heavy metals by the inhabitants is occuring.

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SOME BIOTECHNICAL POSSIBILITIES OF REDUCING SOIL AND WATER CONTAMINATION BY NITRATES

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SUMMARY

Contamination of human environment is steadily increasing, despite world-wide actions for its reduction. Recent problems relate to soil degradation and groundwater contamination by nitrates. It is well known that technogenic contamination of natural ecosystems by acid rains and other anthropogenic factors leads to soil degradation. The issues of degradation and of soil fertility call for more attention and offer a promising research areas to all scientific disciplines that study the soil and water as component parts of the agro-ecosystem. As soil and water contamination by nitrates (NO_3^-) is one of the greatest problems of our time, we have chosen it for the subject of our investigations.

Efficiency of special natural substrates (SPS)* was evaluated in exact fertilization trials by comparison with the standard materials used in liming and mineral fertilization. The trials were set up on different kinds of acid soils (pH 3.8-5.8) and wheat, soybean and maize (in crop rotation) were used as test crops. The neutralization and fertilization value of SPS was determined in view of raising the productivity of acid soils by different doses of SPS and mineral fertilizers.

Application of the natural mixture for neutralization and fertilization, the silicate-carbonate based SPS improves the quality of degraded soils, which results in increased yields of agricultural crops, raises soil productivity and reduces contamination hazards in the soil and, thus, also of the plant material and of groundwater. Soil treatment activities insoluble soil supplies and, if there are not any, SPS raises the concentration of macro and microelements as well as organic substances indispensable for a normal development of field crops. SPS also reduces the active acidity of the soil, while considerably improving its microbiological activity, notably the desirable microbiological processes in the soil. Therefore, the problem of fertilization, specially mineral fertilizer

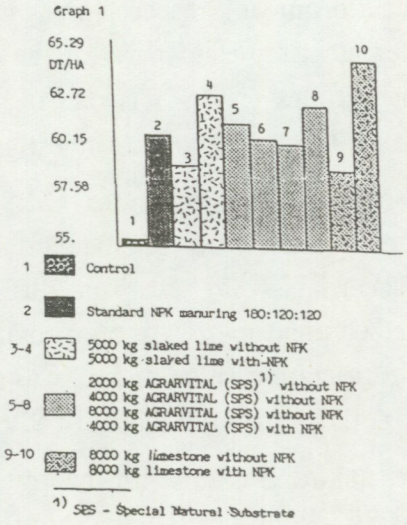
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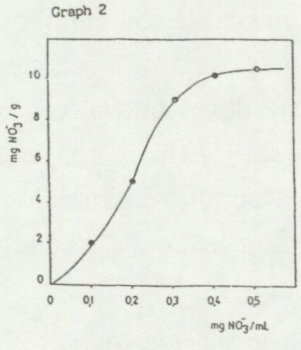
* SPS = a special natural substrate on a silicate carbonate basis

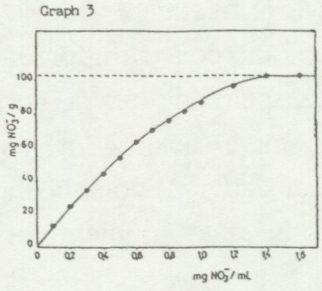
application, notably nitrogen and phosphorus, can be solved by activation of natural supplies and the microbiological processes in the soil. Graph 1. Results of maize yields in different soil treatments. Besides the silicate-carbonate component, SPS contains also other macro and microelements from tuff (volcanic ash), as well as organic substances with Azotobacter sp. Investigation results have shown that the application of SPS in fertilizing reduces the requirements for nitrates by 30-50%.

Parallel to these investigations, utilizing natural mineral substances and ionic exchangers, we have developed a technological process for depuration of drinking water from nitrates. Graph 2. Efficiency of depuration (NO_3^-) on natural substrate AQUA-VITAL. Graph 3. Efficiency of ionic exchange (NO_3^-) on selective, very alkaline anionic resin.

NO_3^- concentrations of 50-180 mg/l were determined by analyses of over 1000 ml wells of drinking water while the standard proposed by the World Health Organization (WHO) amounts to 25 mg/l NO_3^-.







SULFATE SOURCES IN THE GLACIER LAKES CATCHMENT, SNOWY RANGE, WYOMING

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Sulfate in ecologically sensitive alpine catchments is generally assumed to originate from atmospheric deposition. As a result of fossil fuel burning, anthropogenic activity often enhances naturally occurring sulfate (as H_2SO_4) with the potentially adverse impact of increasing acidity in excess of the buffering capacity of the catchment. Thin, immature soils and chemically resistant bedrock, common in alpine catchments of the western United States, lack the ability to consume excess acidity at a rate equal to that supplied. In order to assess the influence of anthropogenic inputs of SO_4, potential intra-basin sources of SO_4 must first be identified (e.g., sulfide minerals).

Bedrock in the Glacier Lakes (East and West), Snowy Range, Wyoming catchment is comprised of Medicine Peak Quartzite (ca. 85% of area) cross-cut by mafic dikes (ca. 15% area), both Precambrian in age. The quartzite is essentially chemically inert while the mafic minerals (actinolite and epidote) weather in a complex manner. Pyrite is present in the mafic dikes as disseminated crystals and minor vein in-fillings. Oxidation of the pyrite is very active and indicated by the presence of insoluble Fe-oxyhydroxides as weathering replacements. In the West Glacier Lake (WGL) catchment, pyrite-bearing bedrock represents a significant intra-basin source of SO_4, and provides the opportunity to distinguish between bedrock-generated SO_4 and that introduced through atmospheric input.

Stable sulfur isotope analyses of precipitation yield values generally ranging from +3 to $+5^{o}/_{oo}$ while typical sulfide minerals range from -4 to $-6^{o}/_{oo}$. East Glacier Lake has a sulfate isotope signature consistent with precipitation ($+4.1^{o}/_{oo}$) indicating very little influence from bedrock sources. One tributary in the WGL catchment was initially thought to have the least amount of bedrock influence, yet its low positive value ($+0.7^{o}/_{oo}$) indicates bedrock solute sources are important during base flow conditions. Discharge in another WGL tributary is dominated by bedrock circulation as reflected by the negative isotope value ($-2.1^{o}/_{oo}$), and the high concentration of cations indicative of bedrock weathering.

Stable sulfur isotopes represent a powerful geochemical tracer for investigating both natural geochemical processes as well as evaluating anthropogenic influences. In addition, the presence of small quantities of bedrock pyrite reiterates the general observation that solute chemistry in alpine catchments is greatly influenced by often overlooked trace minerals.

THE RELATION BETWEEN THE GEOCHEMISTRY AND THE SENSITIVITY TO ACIDIFICATION IN TILL

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Damages to the environment are increasing in Finland and increasing contents of a number of elements in groundwater has been reported, which indicates increasing leaching of the overburden. These problems are, at least in part, a consequence of acid precipitation. Glacial drift, mainly till, covers most of the country and Precambrian, mainly acid, rocks form the major part of the bedrock. The content of carbonates is very low in the bedrock and most of the overburden is buffered against pH changes by base cations. Therefore, the geochemistry of the fine fraction of till, which exists for most of the contry, might be used as a measure of the sensitivity to acid rain. To study the relation between the geochemistry of till and the sensitvity to acidification some 500 samples were collected. The -0.06 mm fraction was analysed for 30 elements after leaching in aqua regia. In addition, the same fraction was leached in deionized water and in acidified water (pH 4) and the solutes were measured on their pH, conductivity and contents of Ca, K, Mg, Fe, and Mn. The results show a stronger leaching of these elements at pH 4. The sensitivity to acidification decreases with increasing contents of a number of elements in the fine fraction of till. The results indicate that acidification problems can be predicted by the use of regional geochemical maps of the overburden and that leaching is considerably increased in till by water acidified to pH-values common in acid rain.

HYDROGEOCHEMISTRY OF THE DUTCH GROUNDWATER - CLASSIFICATION INTO NATURAL HOMOGENEOUS GROUPINGS WITH FUZZY C-MEANS

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Since 1979 the Dutch National Institute of Public Health and Environmental Protection (RIVM) is establishing the Dutch Groundwater Monitoring Network (LMG). This network consists of about 400 monitoring sites. At each site well screens are placed at two depths (10 and 25 m -ls; respectively shallow and deep samples). Samples are collected every year and are analyzed for electroconductivity, pH, Na, K, Mg, Ca, NH_4, HCO_3, Cl, NO_3, SO_4, H_4SiO_4, PO_4, Total P, TOC, As, Ni, Zn, and extractable and volatile chlorinated organic compounds. Tritium contents have been measured in the first sampling round.

The geochemistry of the Dutch groundwater system is very complex, owing to the varying source compositions (sea-, river- and rainwater), complicated geo(hydro)logy, human impact on flow systems and pollution. The interpretation of the large number of hydrochemical data from such a monitoring network requires some type of structuring. An exploratory approach is to look for intrinsic homogeneous groupings within the data set with each a typical (macro)chemistry, which may serve as a basis for further analysis. The selection criteria for the placement of the monitoring sites of the LMG are mainly based on soil type, land use and to some extent on geohydrological situation. A classification based on the two most reliable criteria, soil type and land use, does not result in distinguishable homogeneous groupings as shown by histograms and Discriminant Function Analysis. Traditional water classification methods are in most cases either too rough, causing loss of information, or too refined, resulting in an unwieldy large number of classes.

Fuzzy C-means clustering has been successfully used to discern the structure in the LMG data of one year and to discover natural groupings. The number of clusters is decided heuristically with the aid of Non Linear Mapping, on the basis of the regional distribution, the hydrogeochemical interpretability and the unimodality of the distribution of the parameters per cluster. The consistency of the model can further be proven by the similarity of the cluster types for the shallow and deep samples, and the reproducibility between different years.

A six cluster model was adopted for shallow samples and will form a firm base for statistical and hydrochemical evaluation of the data. These clusters can easily be related to different geochemical processes, natural watertypes and anthropogenic input: acid 'infiltration' in sandy topographic heights, 'lime' for

PERCUTANEOUS ABSORPTION OF LEAD

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Absorption of inorganic lead salts through the skin has been regarded as negligible. Research by CSIRO has shown, however, that many inorganic lead salts are skin absorbed, and that even some water insoluble forms of lead such as lead metal or lead oxide powders dissolve in sweat and pass through the skin. In the early research, skin absorption of lead metal placed on the right arm caused elevated levels in sweat and saliva in the left arm after only 2 hours, but no significant increase in blood or urine lead was detected using anodic stripping voltammetry (Lilley et al, 1988; Anon, 1989; Florence et al., 1988).

In the current experiments, 5mg of 204-enriched lead as nitrate (66% ^{204}Pb cf ~1.4% natural abundance) was placed on one arm and blood (for whole blood and plasma determinations), urine and sweat samples taken from the other arm after various times. Lead contents and lead isotopic compositions were measured using thermal ionisation mass spectrometry.

Mass balance measurements showed that of the original 5mg of lead applied to the arm, 1.5 mg was absorbed through the skin. The total lead content of urine and whole blood showed no measurable increase but absorption was clearly detected in the isotopic composition of the urine after ~ 5 hours and ~ 6 1/2 hours in the whole blood.

Skin-absorbed lead obviously behaves differently to intravenously injected or ingested lead with respect to uptake, partitioning and movement within the body.

The occupational hygiene implications of percutaneous absorption of lead are profound. Few precautions against skin exposure for workers are taken in the lead industry. Furthermore, our research shows that lead absorption through the skin cannot be detected by increases in lead content of blood (or urine), the main criterion by which the industry determines exposure.

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RELEASE AND TRANSPORT OF ALUMINUM SPECIES RESULTING FROM PROTONE BUFFERING PROCESSES IN ACIDIFIED FOREST SOILS

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This investigation deals with the influence of different loads of protones on the release of aluminum in acidified forest soils typical for the Hamburg area. The soluble species of aluminum released by the process of H^+-buffering are of great importance for the mobilisation and transport of aluminum and must be taken into consideration.

It is well known that buffer reactions take place on the walls of the soil pores and therefore the aggregate surfaces show stronger acidification than inner parts of the aggregates. That is why the subject of investigation must be the soil solution produced by percolation of undisturbed soil samples where natural waterflow conditions are simulated. The choice of research sites due to different grain size distributions characteristic for the analysed soils considers the influence on exchange and buffer reactions caused by different pore systems.

Undisturbed soil samples are percolated by solutions of different acidity (pH 2.8, pH 4.2) until a chemical equilibrium is reached between exchange sites and percolating solution. In addition canopy throughfall water collected at research sites is used to produce the "equilibrium-soilpore-solution" by this percolation method. The use of an cation exchange method (modified Driscoll-method) allows the separation of organic and anorganic aluminum forms. The distribution of anorganic aluminum species is calculated by use of computer modelling (PHREEQE by D.C. Parkhurst et al.).

Obviously a low H^+-load favours aluminum transport in association with dissolved organic carbon (DOC). This also is valid for sandy soils poor in anorganic exchange sites depending on the content and the solubiltiy of organic sub-

stance. The more the soil is loaded with protones the more aluminum is transported as anorganic species whereas the content of DOC in the soil solution does not change worth mentioning. The amount of total aluminum released by buffer reactions is strongly correlated to the level of H^+-load.
In general the buffering of high H^+-input is astonishingly complete, even in high acidified soils. Low H^+-loading leads to an acidification of pore water due to the relative high water offer. This is caused by dissolution of organic acids, dissociation of neutral salts and hydrolysis of metal cations.

The application of ICP-MS in environmental monitoring.

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Inductively coupled plasma mass spectrometry is a relatively new analytical technique; the first commercial instrument was available in 1983. This instrument uses an Ar plasma as a high temperature (8000 K) ion source, capable of producing positive ions from most chemical elements. The hot plasma gases, together with entrained sample ions, are extracted via an interface into a quadrupole-based mass analyser. The ICP-mass spectrometer (ICP-MS) combines the characteristics of very low limits of detection, multi-element capability, wide dynamic range and rapid sample throughput. Because the instrument uses a mass analyser it has the added advantage of providing isotopic information.

In this paper we describe some of the wide range of applications of ICP-MS in environmental geochemistry. The instrument described is capable of analysing aqueous samples introduced into the plasma via a nebulizer/aerosol system. In this mode any samples can be analysed provided that they can be prepared as aqueous solutions. In addition to this mode of analysis our instrument is equipped with a laser ablation system. In the laser ablation mode solid samples are subjected to intense laser pulses causing some of the material to be removed (ablated) from the surface. Fragments of sample, typically of 3-5 um diameter, are transported to the plasma by a stream of Ar where ionization takes place.

Analysis of a number of sample types will be described.

1) Waters.

The ICP-MS is ideally suited to the analysis of waters. Because of the very low limits of detection analyses can be performed without the lengthy pre-concentration required for many other techniques. Samples can be analysed every 3 minutes and it is possible to switch from highly contaminated mine waters to potable water within a matter minutes. Under ideal conditions the detection limit for the most sensitive elements e.g. U and Th is around 0.001 ug l^{-1} whilst the majority of elements can be detected at the 0.01 ug l^{-1} level. The instrument has been used to monitor Al, Pb and Cd in potable/ground waters. We have used ICP-MS for the characterization of aquifers used for bottled mineral waters and studied the hydrochemistry of mine waters (c.f. Fuge *et al*. this meeting).

2) Soils/stream sediments/estuarine muds.

These samples can be analysed in a solution form following either partial extraction or total acid digestion. Taking into account the normal dilution factors the detection limits in the solid are still better than 1 ug g^{-1} for many elements. Most of the solution preparation techniques employed in this type of work involve heating the sample, with the risk of loss of volatile elements e.g. Hg. In this paper we describe the calibration and use of a laser ablation system for the direct analysis of such solid samples.

3) Vegetation.

This type of sample material can be analysed in solution form following one of the normal digestion procedures. Again there is is the risk of loss of volatile elements during dry ashing. We describe preliminay work on laser ablation ICP-MS of vegetation samples produced as pressed discs.

The ICP-MS has obvious advantages as an analytical tool in environmental geochemistry. Because of the detection limits routinely achieved we are, for the first time, in a position to establish true background levels for a wide variety of trace and ultra-trace elements in the natural environment.

THE USE OF HARD PART CHEMISTRY OF MODERN SHELLY ORGANISMS IN MONITORING ENVIRONMENTAL CHANGE.

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This paper describes the use of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in the analysis of carbonate shell material. Laser ablation allows solid materials to be sampled directly, removing the need for sample digestion, and provides the added advantage of spatial resolution of around 150 um. The ICP-MS is capable of rapid multi-element analysis with very low limits of detection. The instrument is calibrated using synthetic multi-element standards and thus the data obtained are quantitative.

LA-ICP-MS has been applied to a study of the spatial variation of some minor elements (including Mg, Mn, Zn, Sr and Pb) in the hard parts of a variety of modern shelly organisms. Marine shell chemistry is often used to monitor changes in environment. Bulk shell Mg/Ca ratios are used to place estimates on temperatures and Sr/Ca ratios reflect the salinity of the water at time of growth. By analogy fossil shells have been used to estimate palaeoenvironmental conditions. It has also been suggested that modern shells may be used as monitors of heavy metal pollution.

Filter feeding bivalves *Arctica islandica* (the Iceland cyprina) and *Mytilus edulis* (the common mussel) were collected from Cardigan Bay, an embayment of the southern Irish Sea. *Arctica islandica* shows 2 distinct shell regions, an inner layer with about 2800ppm Sr and 210ppm Mg; and an outer layer with about 1100ppm Sr and 110ppm Mg. Within layer variation is up to +/- 6% for Sr and +/- 30% for Mg. *Mytilus edulis* shows an inner white layer with about 860ppm Sr and 140ppm Mg whilst the outer, dark blue portion of the shell contains about 625ppm Sr and 600ppm Mg. Growth bands within the inner layer of *Mytilus edulis* show a superimposed variation of up to +/- 50%. Cardigan Bay is known to be Pb-Zn polluted and both shells show high Pb contents (*Arctica* up to 30ppm and *Mytilus* up to 15ppm) which is typically concentrated in discrete layers.

The gastropod *Patella vulgata* (common limpet) shows seasonal growth bands with a cyclic variation in Sr (1200 to 1320ppm) and Mg (3000 to 5000ppm). Low levels of Pb (between 1 and 5ppm) also reflect this variation with higher Pb correlating with high Mg. Other gastropods such as *Nucella lapillus* (common dog whelks), *Gibbula umbilicalis* (purple top shells) and *Littorina littorea* (common periwinkles) also show highly variable Sr/Ca and Mg/Ca ratios (occasionally near an order of magnitude) but all generally contain <5ppm Pb.

Zn and Cd are typically concentrated in the soft parts and are as yet undetected in any of the shells studied.

Clearly bulk shell material is highly variable in its chemistry and will thus only provide an averaged estimate of environmental conditions. The spatial analysis and sensitivity offered by LA-ICP-MS allows seasonal variations to be monitored.

THE GEOCHEMISTRY OF CADMIUM IN THE SECONDARY ENVIRONMENT IN THE VICINITY OF ABANDONED METALLIFEROUS MINES IN WALES.

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Wales has a long history of metalliferous mining and all of the ore fields are littered with abandoned mines and spoil heaps, many of which are very extensive. While several metals were extracted, including gold, the major metals sought were copper, lead and zinc. Most of the ore minerals are sulphides, zinc occurring as sphalerite in which cadmium is also ubiquitous. Analyses of ZnS from the region reveal Cd levels of up to 0.5% with Zn/Cd ratios ranging from about 120 to 350.

Heavily contaminated soils in the immediate vicinity of spoil heaps can contain over 1000 ppm Cd, the Zn/Cd ratios generally in the range 100 to 300. Soil cadmium contamination resulting from spoil has been found to extend for several kilometres, with some alluvial valley soils in agricultural areas frequently containing 10 to 50 ppm and occasionally more than 100 ppm.

Adit and spoil drainage waters in the region have also been found to be heavily contaminated, with cadmium levels of up to 1 mg/l in surface waters and 2.7 mg/l in ground waters. The Zn/Cd ratio of these waters is very variable ranging from about 20 to 800. In the vicinity of the spoil tips the Zn/Cd ratio of ground waters is generally lower than 100 while surface drainage waters in the same areas tend to exhibit ratios of between 100 and 250, which is also the case for most adit drainage waters. However, it has been found that adit waters which are rich in iron and tend to precipitate ochre have relatively high Zn/Cd ratios, typically 400 to 800. It is suggested that the cadmium content of the drainage waters is controlled by oxidation with consequent precipitation of Fe which scavenges Cd.

The Cd content of tip and adit drainage shows marked seasonal variation with the highest levels being recorded in the Winter period. However, the Zn/Cd ratio of individual streams shows remarkable temporal constancy.

MEASUREMENTS AND STEADY-STATE MODELING OF BIOGEOCHEMICAL PROCESSES AT THE SEDIMENT-WATER INTERFACE OF EUTROPHIC LAKES

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In the sediments of eutrophic lakes, the major part of the organic material is decomposed in respiration processes at the sediment-water interface. The anaerobic processes at the sediment subsurface produce reduced chemical compounds like methane, ammonium, hydrogensulfide, iron(II) and manganese(II) ions.

As a method of lake restoration, O_2 is introduced into the hypolimnion of several Swiss lakes. A very steep redox gradient is the result of the oxidation of the above mentioned decomposition products. The analysis of flux measurements by benthic chambers and dialysis pore-water samplers in lake Sempach (Switzerland) has demonstrated that the zone with the main activity in the sediments is limited to the top few millimeters. The high diffusion fluxes through the sediment-water interface are caused by intensive microbial oxidation processes in the lake water above the sediment and by equally intensive microbial reduction processes in the pore water of the sediments. During autumn and winter, the majority of these processes approach steady-state conditions.

Most available models on transport and chemical reactions are restricted to few compounds and neglect the role of chemical speciation. However, from calculations of the phosphate speciation in the pore water of lake Sempach, we estimate, that about 30% of the dissolved phosphate is present as metal complexes, thus the diffusion of phosphate is significantly related to the diffusion of calcium.

In order to consider simultaneous occurrence of complex formation, diffusion and microbial processes, we have developed a computer program which is based on a steady-state algorithm. The top five millimeters of the sediment are divided into five compartments. One of the following processes dominates the redox transformation in each compartment: oxidation of organic matter with O_2, NO_3^-, SO_4^{2-}, MnO_x and FeOOH. The material exchange between the compartments is determined by diffusion processes. The input parameters of the program are the rates of the microbial processes (obtained from flux measurements), the stability constants of the equilibrium reactions and the molecular diffusion coefficients for each chemical species. The solution of the steady-state problem provides the full chemical speciation in the five compartments and the diffusion fluxes of C, N, S, P, Mn, Fe, Ca and Mg across the sediment-water interface.

USE AND LIMITATIONS OF GEOCHEMICAL-MASS-TRANSPORT CODES AT A SITE OF GROUNDWATER CONTAMINATION BY ACIDIC WASTEWATER

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Heavy metals (Cu, Co, Ni, Cd, Mn, Fe) are prevalent in groundwater and surface water contaminated by acid drainage from mining activities throughout the world. The chemical evolution of acid-contaminated groundwater at the Pinal Creek toxic-waste site in Arizona cannot be simulated realistically by current contaminant-transport computer codes. The Pinal Creek site serves as an example of the capabilities and limitatations of PHREEQM and MST1D, two computer codes capable of simulating the transport of contaminants affected by aqueous-speciation and mineral dissolution/precipitation processes. MST1D and PHREEQM both offer significant improvements over the capabilities of traditional advection-dispersion codes. Our simulation of the Pinal Creek site considers the evolution of 14 aqueous components, including pH and pe, with possible equilibration of up to 9 minerals.

The results of the PHREEQM and MST1D simulations are similar, and thus impart some confidence in the numerical accuracy of both transport codes. Although PHREEQM and MST1D both use the mass-transfer program, PHREEQE, to solve chemical equilibrium equations, their transport algorithms differ considerably. PHREEQM is based on a mixing-cell model, whereas MST1D uses a finite-difference numerical simulation. PHREEQM currently contains more geochemical options than MST1D, such as ion exchange and time- and space-dependent input/output of reactants external to the groundwater system. The chemical front positions predicted by MST1D are more accurate than those predicted by PHREEQM because of the capability of MST1D to iterate sequentially between transport and chemical equilibration. However, to avoid numerical dispersion problems, MST1D requires a small time and space discretization. MST1D has a more flexible set of boundary condition options than PHREEQM and, generally, has a more customizable flow model. Although the MST1D and PHREEQM simulations were not conducted on the same computer, PHREEQM is not as computationally intensive as MST1D. This results from PHREEQM's lack of sequential iterations and its ability to use a large timestep without numerical dispersion problems. Both codes can run complex simulations on workstation-class computers.

PHREEQM and MST1D can be used to help understand the geochemical evolution of contaminated groundwaters, such as those found at the Pinal Creek site. Nevertheless, a realistic simulation of the Pinal Creek site is currently not possible. The high groundwater velocity (5 m/d) at the site invalidates the assumption of local equilibrium, which is used by both PHREEQM and MST1D.

Effects of Acid Load on Leaching Forest Soil Columns Amended with Lime and Phosphorus: I. Chemical changes

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ABSTRACT

Acid loading of forest soils has accelerated the leaching of plant nutrients. The use of lime and lime combined with calcium phosphate in mitigating the impact of acidic deposition was suggested. A laboratory experiment was performed to investigate the downward effects of $CaCO_3$ and $Ca(H_2PO_4)_2.H_2O$ (separately and in combination) in soil columns leached with pure water and different acid solutions at pH 3.7 (H_2SO_4, and H_2SO_4+HNO_3 at two molar ratios, 1:1 and 1:2). The soil columns were composed of three different layers (0-5, 5-10, 10-25 cm) simulating the vertical distribution of top horizons collected from a forest soil profile in Hasslöv (South Sweden). The amendments were mixed into the top 5 mm of the mor humus layer, at a rate of 5 $t.ha^{-1}$ for lime, and 332 $kg.ha^{-1}$ for calcium phosphate. Three replicates were used in all treatments. The columns were continuously supplied with pure or acidified water at an average rate of 12 mm.d-1 for 8.5 months. This intensive leaching (>3000 mm) was intended for projecting possible long term effects (5-10 years). At the end of the experiment, the columns were dismantled into 5 cm thick layers and analysed for different properties.

Lime was not completely dissolved at the end of the experiment in spite of the large amount of leaching solution. Simulated acid rains and pure water induced similar effects on soil pH, indicating very high buffering capacity in the top humus horizon. However, soil pH was increased down to 10 cm in the limed columns. Calcium enrichment due to liming was noticed down to the same depth as the changes in soil pH. Anion dynamics clearly affected the quantitative accumulation of exchangeable Ca in the top layers. Under leaching with pure water or with H_2SO_4 (sulphate anions being partly retained in the upper soil), Ca tended to accumulate in the top layers. When NO_3 was present in the leaching solution, solubilized Ca was less retained and transported down with the very mobile nitrate anion.

Liming resulted in a dramatic Mg depletion. This detrimental side-effect might be reinforced by rain acidity. Calcium phosphate also induced slight Mg removal from the top horizon. Amendments containing Mg could be suggested as preferable liming material. In all treatments, exchangeable K was greatly exhausted in the upper horizons. This likely results from lowering the ionic strength in the soil solution. Similarly, almost complete Na removal was noticed. These last observations draw attention to the possible depletion of vital nutrients which are generally not included in the amendments.

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Modelling the Chemistry of Humic-Rich Soil Leachates

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ABSTRACT

During the course of a long-term laboratory study in which variously-amended forest soil samples are being leached with different solutions, a large number (193 sets) of chemical analytical data on the leachate solutions have been obtained. The chemical data have been used as inputs to a humic ion-binding model (model IV) in order to test its performance with respect to (a) ionic charge balance, and (b) the prediction of solution pH. In model IV the humic substances are assumed to bear discrete sites, able to bind protons and metal ions (mainly Al3+ and AlOH2+ in the present case). The model takes into account electrostatic effects associated with the variable net charge on the humic molecules. The model as used in the present work had been optimized with laboratory data, and with field data for surface waters; no parameter adjustment was applied to fit the leachate data.

To assess ionic charge balance, measured pH is used as one of the inputs for model calculations, the net humic charge is computed, and used to calculate the ratio of positive to negative charge in each solution. This gave a mean charge ratio of 1.07 (standard deviation 0.52) for the complete data set, and a ratio of 1.01 (s.d. 0.23) when 8 obvious outliers were omitted. If humic substances were ignored in computing charge balance, a mean ratio of 4.61 (s.d. 3.98) was obtained.

To calculate pH, total concentrations of strong acid and strong base were required as inputs. On average, the calculated pH exceeded the measured value by 0.1 pH units, with a standard deviation of 0.9 pH units; the corresponding values if humic control of pH was ignored were 1.7 and 2.0 pH units respectively. Much of the discrepancy between measured and calculated pH when the model is applied reflects analytical errors in the input values.

The model calculations indicate that aluminium in the leachates is largely bound by humic substances; in 89% of the leachate solutions, Al is calculated to be > 90% humic-bound.

INFLUENCE OF SOIL TYPE ON Cu AND Cd TOXICITY FOR PLANTS

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A previous experience, presented at the International Conference on Metals, held in Florida (USA, 1990), showed that the response of the alfalfa plants to Cu-enriched soils varied according to soil nature. In ten artificially Cu-fortified Chilean soils, it was verified that the Cu-upper critical level (Cu-UCL) was maximized in soils with abundant 2:1 clay minerals, especially montmorillonite, high organic matter contents and/or high Ca contents.

The research was continued with a new pot-experiment designed to determine the Cd-UCL for alfalfa plants in six experimentally fortified Chilean soils, carried out under uncontrolled greenhouse conditions, at La Platina Experimental Station (Metropolitan Region). After finishing, soils were submitted to metal sequential extractions, using water, 2.5% v/v acetic acid, 1M KNO_3, 0,1M Na-pirophosphate, 0,05M Na-EDTA and conc. HNO_3 in that order.

Besides the fact that Cd was largely more toxic for alfalfa than Cu, it was verified the UCL values of both metals changed from soil to soil following the same pattern; therefore, the same soil held the highest Cu- and Cd-UCL.

It was detected that Cu-UCL values were directly related to the sum of the fractions extracted by Na-pirophosphate and Na-EDTA, expressed both in relative terms of total extraction, specially to the Na-pirophosphate one; as EDTA was applied after Na-pirophosphate, the results do not invalid the use of Na-EDTA as predictor of Cu affinity by soils. On the other hand, Cu-UCL were reversely related to the KNO_3-Cu.

Added Cd followed a rather similar pattern than Cu as the same associations between Cd-UCL values and extracted fractions, expressed in relative terms, were obtained; however, association with Cd-EDTA and Cd-KNO_3 were better defined.

Na-pirophosphate, Na-EDTA and KNO_3 are supposed to extract the organically retained, non-specifically sorbed and exchangeable metal fractions. So, the results indicates that the Cu/Cd affinity of soils must be directly estimated by the contents of organic matter and clay minerals dominated by pH-dependent charges; reversely, a poor affinity should be expected if a soil has high permanent charge-dominated clay minerals.

ORGANIC MATTER, IN RELATION TO Cu AND Cd TOXICITY FOR PLANTS

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A pot-research to determine the effect of organic matter amendments to quartz sand, experimentally fortified with Cu or Cd, upon the growth and nutritional status of Medicago sativa plants, was carried out in 1990 under uncontrolled greenhouse conditions at La Platina Experimental Station (Metropolitan Region). Metals were added to sand as aqueous solutions of $CuSO_4$ or $CdSO_4$ in doses to get 0, 250, 500 and 800 mg Cu per kg and 0, 50 and 125 mg Cd per kg; it was assumed that the metals remained in available forms.

The addition of compost to the metal-fortified sand reduced the deletereous effects upon plant growth induced by the excess of available metals, allowing a better expression of their growth potential. Thus, the organic matter increased the Cu and Cd upper critical levels (UCL), from 46 and 29 mg kg^{-1} to 372 and 95 mg kg^{-1} sand, respectively.

Those plants cultivated in pure metal-fortified sand showed increased contents in the aerial tissues of the respective added metal, with increase rates directly related to the level of addition. Significant differences in the additional uptake of both metals were measured: whereas Cd content dramatically increased from <0.1 to 5.6 mg kg^{-1} d.m. at the treatment of 50 mg Cd kg^{-1} sand, Cu content was lightly but consistently increased from 10 to 13.4 mg kg^{-1} d.m. at the treatment of 500 mg Cu kg^{-1} sand. As result of compost amendments, the rate of additional accumulation in the aerial tissues was significantly reduced to 3.1 mg Cd and 11.9 mg Cu kg^{-1} d.m., at the same level of Cu or Cd additions to sand, respectively.

When cultivated in pure metal-fortified sand, antagonistic effects upon Mo and Zn contents in the harvested green tissues were detected. Mo content decreased from 6.8 to 2.0 mg kg^{-1} d.m. in presence of either Cu or Cd; Zn content was reduced from 26.3 to 22.7 mg kg^{-1} d.m., in presence of Cu, and to 18.3, in presence of Cd. Amending the metal-fortified sands with organic matter, the depletion of Zn and Mo contents in the aerial tissues were completely buffered for the cupric treatments, whereas there was a significant reduction in the rate of depletion for the cadmic ones.

MAPPING OF HEAVY METALS IN SHALLOW COASTAL AREAS.

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During many years, the discharge of heavy metals from industries around the big city regions have been accumulated in the sediment. Higher aquatic plants, i.e. macrophytes, may colonize the bottom sediments if the plant available fraction of heavy metals is not too high or if new unpolluted sediment has been deposited on top of the old contaminated sediment. Plant roots were shown to penetrate up to 0.5 m into the sediment and take up heavy metals and transport them further up to the shoots. Thus macrophytes may be valuable tools when mapping the pollution in shallow coastal areas.

When using macrophytes for this purpose, however, a few points have to be taken into consideration. Different plant species were shown to take up different amounts of heavy metals and transport metals from root to shoot to varying degrees. This stresses the importance to use identical species of plants to be able to compare the data. The character of the sediment is also of importance. The plant available fraction of heavy metals in the sediment was found to increase with decreasing amounts of organic matter. Also the pH, redox-potential and salinity can affect the uptake of heavy metals. Roots of aquatic plants were found to be able to lower pH and increase the redoxpotential and thereby increase the metal fraction available to the plants. Aquatic plants are also able to absorb elements via the shoots directly from the water. The uptake by aquatic plants can thus be used as an indicator of the amounts of metals which are available for biological system.

As an example we present data from a study where heavy metals were mapped in the shallow coastal areas in the Baltic archipelago of Stockholm.

GEOCHEMICAL INFLUENCE OF MINING ACTIVITIES ON THE ENVIRONMENT

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From the ecological point of view the ore deposits and their primary geochemical halos are naturalsources of many chemical elements and the zones of their impact on biological systems are determined by landscape-geochemical features of ore-mining regions.In ore-mining regions man-made(technogenic)geochemical anomalies are very abundant too(alongside with the natural anomalies - primary geochemical halos and secondary dispersion halos in soils and waters). Geochemical research of environment in the ore-mining regions have to precede the economic development of a territory since they enable predictions of impact to be made as well as to provide the actual materials for the planning of facilities. In the processeof development the operations have to be continued with the aim of evaluating the impact and devising measures on reducing inevitable negative influence of the ore-mining facilities upon the environment. To be cited as an example are the results of the geochemical research carried out in the area of the Alaverdi mining and metallurgical works in the Armenian Republic. Detailed geochemical sampling of soils, plants and rivers has established a high degree of environmental pollution in the area by chemical elements, primarily copper, lead, zink, cadmium, antimony, arsenic and molybdenum.The impact of the Alaverdi works through ejections in the atmosphere extends to 3-5km and to dozens of kilometers(sampling different species of plants) has established in the zone of maximum environmental pollution I.5km around the works high concentration levels of polluting elements in vegetation.

THE CONTRIBUTION OF TIN-LEAD CAPSULES AS A SOURCE OF LEAD IN WINE

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The lead isotope fingerprinting method has been used to determine whether soluble lead compounds produced by reaction of wine with tin-lead capsules are drawn back through and/or around corks to give an apparently elevated lead content in wine.

Lead isotope abundances and precise lead concentrations have been measured in wines, corks and capsules for over 50 bottles of mainly Australian and a few German wines. To minimize variables such as soil type and winemaking procedures, most samples are from the one vineyard covering a 15 year period. The sample population is biased towards a "worst-case" scenario in choosing a larger number of bottles with significant corrosion and possible cork damage.

Lead contents and isotopic values of the wine and corks are critically dependent on sampling procedures, so that for example, higher lead contents are recorded for decanted samples which had limited cleaning of the bottle neck and cork.

Lead contents of the Australian wines are generally low in the range of 20 to 60 µg/L. The lead isotope values are uniform for separate bottlings within a vintage but show variations both between bottlings of the same vintage; the variation between vintages are attributed to winemaking procedures.

When sampled rigorously, we find no correlation between the lead isotope values in the wine and capsules nor a correlation with isotope values and the degree of capsule corrosion. Furthermore, there is little difference in the isotopic values of wine from lead-capsuled and uncapsuled (or plastic capsuled) bottles of the same vintage. These results provide strong evidence that there is no migration of lead corrosion products back into the wine.

Cork profiles based on analyses of the top, middle and bottom of corks are complex depending on the methods of cork extraction and its preparation for analysis. With extraction by wine freezing and removal of the "rind", there is no evidence for lead migration through the cork. Limited lead migration over a distance of about 2 mm in the top of the corks is detectable in bottles whose capsules are severely corroded. Similarly, in corks with very low levels of lead (<0.2 mg/kg), the lead in the bottom 1-2 mm may equilibrate in time with that in the wine.

To minimize lead ingestion it is recommended that if the capsule exhibits moderate to severe corrosion, the top of the bottle and cork be vigorously scrubbed and rinsed with water prior to corkage and that the lower part of the cork remain unpierced.

If the cork is in good condition, lead in wine from capsule corrosion is not a problem.

PERCUTANEOUS ABSORPTION OF LEAD

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Absorption of inorganic lead salts through the skin has been regarded as negligible. Research by CSIRO has shown, however, that many inorganic lead salts are skin absorbed, and that even some water insoluble forms of lead such as lead metal or lead oxide powders dissolve in sweat and pass through the skin. In the early research, skin absorption of lead metal placed on the right arm caused elevated levels in sweat and saliva in the left arm after only 2 hours, but no significant increase in blood or urine lead was detected using anodic stripping voltammetry (Lilley et al, 1988; Anon, 1989; Florence et al., 1988).

In the current experiments, 5mg of 204-enriched lead as nitrate (66% ^{204}Pb cf ~1.4% natural abundance) was placed on one arm and blood (for whole blood and plasma determinations), urine and sweat samples taken from the other arm after various times. Lead contents and lead isotopic compositions were measured using thermal ionisation mass spectrometry.

Mass balance measurements showed that of the original 5mg of lead applied to the arm, 1.5 mg was absorbed through the skin. The total lead content of urine and whole blood showed no measurable increase but absorption was clearly detected in the isotopic composition of the urine after ~ 5 hours and ~ 6 1/2 hours in the whole blood.

Skin-absorbed lead obviously behaves differently to intravenously injected or ingested lead with respect to uptake, partitioning and movement within the body.

The occupational hygiene implications of percutaneous absorption of lead are profound. Few precautions against skin exposure for workers are taken in the lead industry. Furthermore, our research shows that lead absorption through the skin cannot be detected by increases in lead content of blood (or urine), the main criterion by which the industry determines exposure.

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EXPERIMENTAL SIMULATION OF REDOX PROCESSES IN GROUNDWATER-INFILTRATION SYSTEMS

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Organic matter degradation is the predominant process during the early groundwater recharge. The oxidation of organic matter is mediated by microorganisms for which O_2, NO_3^-, MnO_2, FeOOH or SO_4^{2-} act as electron acceptors. These redox processes were simulated by column experiments (diameter 5 cm, length 29 cm, aquifer sand) for which a synthetic groundwater was used. The column contained seven valves where samples could be taken. It was innoculated with a natural mixture of microorganisms prior to the experimental studies.

The separation of the redox processes (as expected from their reduction potentials) was dependent on the concentration of the organic substrate at the inflow of the column. In the case of high concentrations of organic substrate we found almost no separation which can be interpreted by a rapid drop of the redox potential at the inlet of the column. Our results were obtained both during the growing phase of bacteria and under conditions with the population of microorganisms in steady state. For the latter case the concentration profiles were highly reproducible.

Homogeneous reductions: The reduction processes involving dissolved species allow high reaction rates due to the good availability of the reactants. Oxygen respiration and denitrification are relatively fast processes and occur within the first 2 cm of the column. The reduction of sulfate is about a factor of 5-10 slower and is strongly dependent on the organic carbon source. The kinetics of nitrate and sulfate reduction were pseudo first order.

Heterogeneous reductions: The reductive dissolution of MnO_2 and FeOOH is controlled by the available surface area of these solid phases. For both compounds we observed a linear increase (zero-order kinetics) of the M^{2+} concentration as a function of the distance from the inlet of the column. The dissolution of FeOOH is affected by carbonate and sulfide (from sulfate reduction). In sulfide-free systems the formation of iron(II)carbonate controls the total iron concentration. In the presence of sulfide, formation of iron(II)sulfides controls the iron(II) concentration. It could be shown by kinetic modelling that iron(II)-sulfide formed stems primarily from the direct reaction of sulfide with FeOOH. Due to the low concentrations of Mn^{2+}, the reductive dissolution of MnO_2 is not affected by sulfide formation.

An increase in alkalinity was observed. It was attributed to proton consumption during the reduction of nitrate and sulfate and in the reaction between FeOOH and sulfide. The increase of bicarbonate is not due to $CaCO_3$ dissolution by CO_2 since the Ca^{2+} concentration remained constant over the whole column.

INFLUENCE OF SEASON AND SOIL MOISTURE ON THE CHEMISTRY OF A SWEDISH PODZOL

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In the Skogaby experimental area, Halland, Sweden, three adjacent plots in a 20-yr old Norway spruce stand growing on a podzolised glacial till were subject to different precipitation regimes. The dry treatment plot received only a minor fraction of the ambient precipitation during summer (May-October) 1990 through the installation of transparent plastic cover one meter above the ground. One plot was irrigated with surface water from a nearby lake for three consecutive summers (1988-1990) in excess of the ambient precipitation. A third plot was a control. During four sampling occasions in May, July, August and October 1990, two soil samples (each consisting of 11 composited subsamples) were collected in two different parts of each plot. Three soil horizons were studied: the forest floor layers, the top 10 cm of the mineral soil (A/E horizon) and the 10-20 cm horizon (upper Bs horizon). The samples were analyzed for pH, S constituents, Bray-1 PO_4, NaH_2PO_4-extractable fulvic acid (NaPFA), loss-on-ignition, and oxalate-soluble Fe and Al.

The results show few significant ($p < 0.05$, paired t-test, $n = 6$) differences between seasons. In the forest floor, water-soluble sulphate invariably peaked in July and reached a minimum in October, while ester sulphate peaked in October - some inorganic SO_4 was evidently incorporated into esters during late summer. In both mineral horizons, NaPFA reached a maximum in October, suggesting a greater DOC leaching potential in the autumn. The pH appeared to reach a minimum in August. Bray-1 PO_4 decreased during summer, especially in the irrigated plot. The latter two seasonal changes probably reflect biological net uptake.

Three summers of irrigation led to a significantly decreased pH($CaCl_2$) in the forest floor (unpaired t-test, $n = 8$) compared to the other two treatments. However, the pH(H_2O) did not differ. In the mineral soil horizons, pH was highest in the control plot. In the 0-10 cm horizon, the irrigated plot contained a lower amount of water-soluble SO_4 and also of ester-bound SO_4. Possibly, a large net incorporation of SO_4 into C-bonded S forms occurred, triggered by increasing N deposition in the irrigated plot. Alternatively, this result may reflect soil heterogeneity. NaPFA was lower in the control compared to both treatment plots. It was observed that pH($CaCl_2$) and NaPFA was highly correlated ($r = -0.61$ and $r = -0.84$ for 0-10 cm and 10-20 cm horizons, respectively), suggesting that with decreasing pH, an increasing proportion of the soil fulvic acids are present as potentially soluble, weakly sorbed surface complexes.

GROUNDWATER ACIDIFICATION IN SANDUR SEDIMENTS.

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The effect of atmospheric deposition on groundwater acidification were investigated in sandur sediments of Quaternary age. At the Klosterhede plantation a series of boreholes along a groundwater flow line, and from the center to the edge of the forest has been established. Each well is sampled continuously with 40 cm cores from the pedon through the unsaturated zone and one meter into the saturated zone, cores were centrifugated to separate the pore water from the sediment, and each water sample was analysed for; all major cations, Cl, SO_4, NO_3, F, pH, Alk. Inorganic Al and SiO_2.

All data has been modelled with the chemical equilibrium model, WATEQ whitch calculates activities, complexation and saturation indexes for possible equilibrium control by minerals. In order to control our understanding of ongoing acidification field data is modelled with th code PHREEQM, which combines a chemical equilibrium model with a 1-D mixing cell transport model.

The unsaturated zone and the upper parts of the saturated zone in Klosterhede is acid, the lovest pH-values measured in the upper part of the unsaturated zone is 4.2 and the highest value measured one meter below the groundwater table is 4.8. In accordance with these low pH values very high concentrations of dissolved aluminium, up to 22 mg/L, have been observed. The Cation exchange capacity is wery low, generally below 0.5 meq/100g sed. and the basesaturation is from 10 to 25%.The pore water is in equilibrium with two known buffer minerals; Gibbsite in all samples and Jurbanite in samples with pH below 4,5. These two minerals control the pore water pH and dissolved aluminium. Thus buffer processes retard the movement of acid groundwater through the aquifer. The infiltrating water is dominated by sodium and cloride and the concentration varies with time more than 100 %. These peaks of infiltrating sodium exchanges with adsorbed aluminium witch prcipitates as gibbsite and thereby decreasing pH. Because of this ionexchange the lowest pH values are found at the front of the sodium peaks, and because a large fraction of the adsorbed cations are sodium it is impossible to calculate "excess sodium" in these samples.

DETERMINATION OF CONTENTS AND ORIGIN OF SULFUR AND HEAVY METALS IN STREAM SEDIMENTS FROM THE ISOJOKI RIVER, S FINLAND

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From an environmental point of view the Isojoki river is important, because it is one of the still "clean" rivers in Southern Finland. The drainage area of the river is 1110 km^2 in size. The bedrock consists of granitoids with some schists and sandstone, while the overburden is mostly podzolic till and bogs. The anthropogenic influence is restricted to thinly populated agricultural areas and some small-scale industry along the river. The river has by UNESCO been chosen as an object in an international research program, Project Aqua.

The aim of this study was to determine the geochemical patterns formed by mineral stream sediments and whether possible anomalies are of natural or anthropogenic origin. The data can also be used for prospecting. Especially the analysis and occurence of sulfur in stream sediments are very scarcely described in the literature. The sediments were sampled in 1975 and stored until analyzed recently with modern instrumentation. The sediments were sieved and the different size fractions were analyzed.

Several instrumental techniques were used for the chemical characterization of the samples. Sulfur and other main components as Si, Al, Fe, Ca, Mg, K, Na and P were analyzed from the solid samples by energy dispersive X-ray analysis (EDX). The micro-structure of the sediments was studied and the mineral grains identified with the same technique. The sulfur contents were controlled with a spectrophotometric titration procedure. The heavy metals, Cu, Zn, Pb, Fe, Mn and the main elements Ca and P were determined with DC plasma atomic emission spectrometry (DCP-AES) and graphite furnace atomic absorption spectrometry (GFAAS) after dissolution with $HF:HNO_3:H_2SO_4$ (2:1:1) in an autoclave bomb. For mercury analysis a cold vapour AAS technique was used. The analytical methods were tested by analyzing the NBS Standard Reference Material 1645.

The analytical results of the sediment analyses indicate that the river still is relatively unpolluted. Silicate-rich materials dominate in the sediments, which is reflected as high concentrations of Si and Al. The content of organic material was mostly below 5%. The concentrations of S, Cr and Fe was also low. The concentrations of heavy metals varies irregularly but a good correlation was obtained between them. The heavy metal concentration increased with decreasing grain size, being highest in the -120 and -62 µm fractions. Some anomalously high concentrations of heavy metals are of geochemical origin.

The SEM/EDX method opens new dimensions for understanding the distribution and origin of certain elements in stream sediments. The sediments are often heterogenous, consisting of aggregates of mineral grains in a very fine-grained, secondary matrix.Conventional methods of analysis give information about the bulk composition of the sample, but with SEM/EDX it is possible to determine both the composition of the matrix and also to identify and characterize the mineral grains. E.g. small "pearls", about 1 µm in diameter, consisting almost entirely of sulfur, with small amounts of iron, was found. These grains are thought to be formed by micro-organisms. The quantitave determination of sulfur in the stream sediments was successful. In analyses of samples known to contain 1% S, the relative standard deviation was about 2%. For the DCP-AES method the precision was 1-2 %.

In a near future a new sampling program is planned in order to monitor the changes that have taken place in the contents of sulfur and heavy metals in the sediments of the Isojoki river.

ROLE OF PHYSICAL AND GEOCHEMICAL HETEROGENEITY IN THE TRANSPORT AND ATTACHMENT OF BACTERIA IN AN ORGANICALLY-CONTAMINATED, SANDY AQUIFER.

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The proposed use of waste-adapted and genetically-engineered bacteria for in-situ biorestoration of organically-contaminated groundwater has led to increased interest in the geochemical controls of bacterial migration in aquifers. A series of small-scale (6 to 12 m travel distance), natural-gradient tracer experiments was conducted at several locations at the U.S. Geological Survey's Cape Cod Toxic-Substances Research Site on Cape Cod, Massachusetts. The site contains a plume of organic contaminants (treated sewage and industrial solvents) within a sandy, glacial-outwash aquifer. Part of the plume has been instrumented with a 20 by 220 m array of 15-port (depth) multilevel sampling device(s) (MLSD). Changes in the differences in transport behavior between bacteria, bacterial-sized microspheres, and conservative tracer (bromide) were evident among the various conductive layers and geochemically distinct zones within the plume. In one injection experiment, the order in which peak concentrations of the three tracers appeared at a MLSD 6 m downgradient from point of injection clearly varied with depth. At 8.8 m below land surface (bls), peak abundance in breakthrough of bacteria (0.2 - 1.4 μm, 0.6 μm mean cell length) was coincident with that of the microspheres (0.7 μm diameter). However, both microspheres and bacteria were retarded with respect to bromide (retardation factor, RF = 1.7). At 9.0 m bls, the bromide and bacterial breakthrough patterns were quite similar, both exhibiting single peaks. However, the bacterial peak preceded that of bromide (RF = 0.8), but the microspheres were substantively retarded (RF = 1.5). Finally, at 9.5 m bls, the pattern of breakthrough for all three constituents were similar, i.e., all exhibited single peaks that were coincident and similar in shape.

Sorption was the largest control of bacterial transport in the small-scale experiments and often accounted for more than a ten-fold reduction in abundance of unattached bacteria within 10 m of travel. The effects of grain surface heterogeneity and groundwater chemistry upon sorption of indigenous bacterial populations onto aquifer sediments were investigated in the lab using small (20 cc) columns. Substantial differences were observed in the pH-dependency of bacterial sorption when the suspending medium was changed from uncontaminated to contaminated groundwater. This suggested that the sharp vertical gradients in chemistry, observed in the region of the tracer tests, may differentially affect the sorption behavior of the bacteria travelling at different depths. The presence of iron oxyhydroxides on grain surfaces substantially enhanced fractional adsorption of bacteria that were suspended in uncontaminated groundwater, but had little or no effect upon sorption of bacteria suspended in contaminated groundwater. There was also a two-fold variation in the extent of bacterial adsorption between experiments employing aquifer sediments collected from outside and from within the contaminant plume. Results from both field and laboratory experiments suggest that the effects of physical and chemical heterogeneity (grain size distribution, preferred flow-path pore structure, ground-water chemistry and mineralogy) must be considered when modeling small-scale transport of microorganisms, and in describing the role of bacterial transport in geochemical processes occurring within contaminated aquifers.

On the theoretical basis of modelling and monitoring of forest ecosystems

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Cultures of ecosystem management through prediction and control are fundamental for any human civilization. Such cultures can be built on i) the accumulated (non-scientific) experience with ecosystems and their past utilizations and on ii) scientific understanding by controlled observations (measurements) on ecosystem structure and function. The management traditions e.g. in forestry or nature conservatiuon are mainly based on the first and much older root of knowledge on biological systems.

Few foresters will claim full understanding of managed ecosystems. The accumulated experience, however, allows reliable predictions e.g. on potential yield far into the future. Forest ecosystems can thus be characterized as poorly understood but highly predictable within respect to their long-term utilization. Such behavior appears to be the contrary of systems ruled by deterministic chaos (well-understood but unpredictable).

Modern risks in forest ecosystem management result indirectly from the large-scale impacts of industrialization. Such risks become manifest as changes in the chemical and physical boundary conditions of forest ecosystems and prominent examples have been termed acid rain or climate change. Changing boundary conditions of forests threaten to devaluate the past experience on which their management has mainly been based.

In science a branch termed ecosystem research has developed in response to these new risks: increased understanding should compensate for lost predictability. Its is, however, unclear at which level of integration this understanding must be sought. Within science measures for the state and dynamics of whole ecosystems do not exist. The prevailing perception of forest ecosystems sees them as a complex interaction of various subsystems or objects that belong into different scientific disciplines. Thus, ecosystem research is regarded as an interdisciplinary task rather than as a science in its own rights (of object and theory).

The response within ecosystem management to the new risks is to seek the necessary additional experience by monitoring of whole ecosystems. Such monitoring assesses the abiotic state of the environment of ecosystems and their boundaries by e.g. meteorology or geochemistry. For the observed or anticipated changes within ecosystems that are relevant for utilization biotic (sensitive species) or abiotic indicators (runoff alkalinity, base saturation in soils, etc.) are sought.

These two parallel approaches yielded variable success: the pragmatic attempt to extent the experience with ecosystems to the changing ranges of contemporary atmospheric loadings by means of monitoring of whole ecosystem experiments can be regarded as successful. Clear empirical and circumstantial evidence links

changes in geochemical and meteorological boundary condition to effects such as water acidification or forest decline. The scientific attempts to establish the causality of such links at the process level, however, must be jugded more critically.

In science no consensus has yet emerged on a theoretical basis in which the observed large-scale effects in forest ecosystems can be explained. This matter is highly controversal. Here it is argued that the obstacle to a scientific understanding at the process level results from the use of inappropriate paradigms. That means the explaining processes might be sought at the wrong level of integration. A critique of these "energy-matter" and "reductionistic" paradigms is attempted and an alternate view exemplified for a simple model of forest growth.

The starting point for an alternate view uses rather old than new ideas and can be summarized by the following items:

- The failure to establish the causality behind forest decline results from an inappropriate theoretical definition of ecosystems and their dynamics.

- An adequate abstraction from (e.g geochemical, hydrological) observations at ecosystem boundaries has to reflect the information aspects in parallel to the energy and matter aspects.

-the process of self-organization as shown by ecosystems might follow exact phenomenological laws.

- Such laws can be used for a rigorous definition of critical loads for whole forest ecosystems.

Two proposed hypothetical laws describe ecosystems as conservative for the algorithmic information content in the irreversible input and output fluxes of matter. One part of the inner information within ecosystem (the biological information) can only increase over time. Such phenomenological laws would be irreducible to the integration level of thermodynamics as they use non-computeable expressions (algorithmic information content).

That means that the question of causality of observed changes can be investigated by sidestepping the much more complicated questions of the reducibility of ecosystems to thermodynamics or the reducibility of life to physics and chemistry. This tentative phenomenology of ecosystems would yield entirely different measures of critical loads when compared to the empirically derived measures that are in use now. For some types of experiments this testable hypothesis would predict an almost opposite response of the biota to the treatment (e.g. in roofed ecosystems).

As data on biological effects of deposition-reduction underneath a roof are not yet available a simple growth model will be used to discuss the different perspectives of ecosystem dynamics.

NITROGEN AND PHOSPHORUS LOSSES FROM AGRICULTURAL LAND: A CATCHMENT-BASED CASE STUDY

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Nutrient losses from agricultural land are dependant upon both the type and intensity of land use. In South West England, livestock enterprises dominate the agricultural sector, with arable production systems being of subsidiary importance. High rainfall and relatively impermeable soils combine to produce patterns of nutrient loss that are markedly different in both timing and quantity from those recorded in arable soils in other parts of the U.K.

Research into problems of nutrient loss from agricultural land has been carried out in the Slapton Ley catchments since the early 1970's. Slapton Ley, which is the largest freshwater body in South West England, has become increasingly eutrophic over the last thirty years. Current annual sediment and inorganic nutrient export from the Slapton Ley catchment is of the order: 6t NH_4-N, 282t NO_3-N, 2t PO_4-P and 1440t suspended sediment. Analysis of the nutrient inputs into the Ley from the contributing catchments has revealed that organic sources of nitrogen and phosphorus have played a major role in the developing eutrophic status of the Ley. Recent research efforts have concentrated the relationship between land use and runoff water quality in small controlled catchment areas. Rainfall simulation experiments (Heathwaite *et al.*, 1990 a,b) suggest that overgrazed permanent grassland is an important source of sediment, total N and total P, resulting in 12x, 9x and 16x the load of ungrazed grassland, respectively. This is due to both increased runoff as a result of surface compaction and increased organic nutrient inputs.

Further work is in progress to evaluate the losses of N and P from grassland that has received large applications of animal waste, in either a liquid or solid form. Again plot based data is being collected, and this will be extended to catchment scale using modelling techniques so that catchment based approaches to controlling nutrient losses can be put forward. This, it is hoped, will lead to improved water quality in Slapton Ley and more efficient nutrient management.

IRON TRANSPORT FROM NATURAL AND MINED PEATLANDS IN THE DRAINAGE BASIN OF THE HUMIC RIVER KIIMINKIJOKI, NORTHERN FINLAND

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Iron discharge and nature of iron-organic colloids has been studied in the drainage basin of the humic River Kiiminkijoki, which crosses an area of minerotrophic mires in northern Finland. The iron transport in a brook draining an area of peatlands still in a natural state, and in peat mining and river water is reported.

Iron concentration and iron content of dissolved organic matter increases under low flow conditions in the brook and peat mining waters, and also in the river. The overall increase in the iron transport due to peat mining is small.

High apparent molecular weight iron-organic colloids are important in iron transport in the drainage basin. The results indicate increase in the formation and mobilization of these colloids in the peatlands of the area following drainage and peat mining. This may be followed by gradual changes in the food webs of the river ecosystem.

PHASE SPECIFIC BONDING FORMS OF HEAVY METALS IN THE SEDIMENTS OF VISTULA RIVER AND ITS TRIBUTARIES

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The ecological risk of heavy metals in aquatic systems are more determined by mobilization than accumulation processes. Heavy metals in sediments and suspended matter are bound in the various components of which these solid phases are composed, i.e. Fe-Mn-oxyhydrates, carbonates, clay minerals, sulfides and organic or biological substances. Among these sediment components clay minerals play an important role in accumulation, sorption/desorption as well as exchange processes of metals.

The contents of heavy metals (Zn, Ni, Cd, Cu, Pb, Cr) in the fraction < 60μm and for selected samples in the clay fraction of different contaminated river sediments were estimated. The metals were extracted from the solid phase with conc. boiling nitric acid, and their contents were determined by atomic absorption spectroscopy. The phase specific forms of heavy metals in the selected samples of sediments were determined using a selective chemical extraction method.

The buffer capacity and the metals mobility after different portions of acid of two high contaminated river sediments was also determined.

The concentration of determined metals is very high and variable, depending on the kind of river sediments and on the metal. The highest content of metals was mesured in the sediments of Vistula, Przemsza and Wilga rivers in the Southern Poland and can reach: Zn 7000ppm, Pb 940 ppm, Cd 200 ppm, Cr 700ppm, Cu 530ppm and Ni 260ppm. The amount of heavy metals in the clay fraction of sediments is occasionally some times higher than in the fraction < 63μm.

Based on the geochemical behaviour of the above metals, they can be subdivided into two groups: (1) highly mobile elements: Cd, Zn, Cu; and (2) metals more strongly combined with the mineral phases of the sediments: Cr, Pb, Ni. Relative portions of exchangeable metals in clay fraction of highly polluted sediments can reach 30% for Zn and Cd; for Ni and Cu 25% of the total concentration of the metals. Cadmium is bound with the carbonatic fraction up to 50%. Above 80% of Cr is bound by poorly crystalline Fe-oxyhydrates, as well as about 50% of nickel and 40% of copper. Zinc and cadmium are mainly combined with the amorphous Mn-oxides. Only a few percent of the total metal concentrations were found in the organic and sulfidic fraction of the sediments. With the exception of Cr and Ni, the lowest portion of metals has been bound in the residual fraction.

The "titration curves" for different suspensions of river sediments show that the presence of calcite is the most important factor affecting the buffer capacity. The sediments of the Wilga river exhibit stronger buffer capacity than those of Vistula river.

GEOGAS IN CRYSTALLINE BEDROCK

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The scientific literature provides conclusive evidence of gas migration through crystalline bedrock and up to the surface. Such gas transfer can alter the chemistry of the rock and possibly also affect the water flow. Furthermore, studies of gas flow may even become a way of gaining more knowledge about the rock itself.

It appears, however, that such implications of gas flow are rarely reported and that data on gas flow, gas composition and flow patterns are scarce or even non-existent.

It is the impression of the authors that this situation may partly be attributed to the absence of a general description of how gas may behave in the rock.

In this paper, a compilation is made of different significant observations of geogas. Based on these observations, and on well-known physical and chemical principles, possible models for the behavior of the gas are analysed and discussed.

Thus, at a depth of some tens or hundreds of meters, the partial gas pressure might exceed the hydrostatic pressure, enabling the development of a gas phase. Such gas may form in fissures in the rock of perhaps 0.1 mm width. The gas deposited will attempt to minimize its surface energy. The shape assumed will thus depend on the geometrical constraints as well as the specific surface energies between gas and water, gas and rock, and water and rock. For a small bubble, or a bubble of moderate size, these effects can be expected to make the bubble stay in place. The accumulation of gas into the gas pocket will imply that a pressure will be excerted onto the uppermost part of the pocket. At some stage of gas accumulation, this pressure will become sufficient for the gas to penetrate upwards through the fissure. As the gas propagates, the hydrostatic pressure decreases and the volume of the gas increases. Eventually, when the surface is reached, a burst of gas may be observed.

Three mechanisms have been identified that may describe how heavy elements can be tranferred from considerable depth to the surface by means of gas. One is the well-known phenomenon of floatation. Another is transfer by elements bonded to complexing agents that are surface active and enrich themselves onto the bubble surfaces. A third mechanism is transportation through volatile compounds that dissolve in the gas.

Finally, the paper makes some recommendations to geoscientists regarding phenomena that may be fruitful to utilize.

DIGITAL SITE CLASSIFICATION - GEOCHEMICAL INFLUENCE ON THE SITE INDEX

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Site classification is a major component in forest management. All planning, operational as well as long term strategical, have to consider the site quality as an important factor to decide the proper actions and timing of actions within a forest estate. The site quality is described by a site index (SI), which is defined as the dominating tree height at a reference age.

In Swedish forestry, two site classification systems exist: (1) The tree height and age are measured and extrapolated to the reference age. This method is accurate but seldom applicable. (2) Given specific site conditions, such as latitude, altitude, ground moisture etc., the SI is estimated through regression functions. This method can be used in all stands. It therefore dominates. It has yet two drawbacks:

- To use the system, it is necessary to stand on the site and make manual measurements. When all site characteristics are measured, the site index is determined through look-up tables. This is ineffective since experienced field personnel are rare and expensive.

- The manual measurements are simplified to fit field conditions and thus include subjective parts, leading to a low precision. Also, the simplified parameters do not downright describe the actual growth potential. The mean error of the estimated growth rate is therefore as high as roughly 20%.

These limitations initiated the Digital Site Classification project, a joint research project at the Departments of Forest Soils and Forest Management. The goal is to determine the growth rate out of digital map information, such as elevation models, soil maps and geological surveys. The attempt is to use already available and objectively measured data, thus avoiding the obstacles in the existing system.

This paper reports on initial studies of the relationships between the geochemical properties of the soil and the site index.

A general and country-wide geochemical survey is undertaken by the Geological Survey of Sweden. Soil samples from the C-horizon of moraines are collected in a systematic grid with approximately 2 km point distance. Contents of 21

oxides and tracers are analyzed. Data from 370 plots were used in this study.

The SI for Pinus silvestris was measured at 326 sample plots and for Picea abies at 318 plots in the district of Hälsingland in central Sweden. The SI was estimated with both existing methods. Kriging interpolation was applied between the geochemical plots to estimate the geochemical properties at the SI plots. Catchment areas to each SI plot was calculated in a digital elevation model. Plots with a catchment area of 0.05-0.3 ha were included in this study in order to avoid plots where water stress or lateral transport of nutrients occur. Correlations between the geochemical properties and the SI was thereafter calculated.

Results show that for Pinus silvestris, 7 of 21 elements had a significant correlation with the SI on 0.1% level. Nine of the elements had a higher correlation with the SI, measured by height/age, than the correlation between the two SI estimations. The correlation increased when only plots on slopes below 5% were used. For Picea abies, no significant correlation was observed.

Conclusions are: (1) Although sparse - the geochemical sample plots contain information about the local SI for P. silvestris. (2) The general geochemical survey can be used as one component in a digital site classification system - at least for P. silvestris.

THE ROLES OF GEOLOGY AND GEOCHEMISTRY IN ESTABLISHING A SITEWIDE SOIL AND GROUNDWATER BACKGROUND FOR ENVIRONMENTAL RESTORATION ACTIVITIES AT THE HANFORD SITE, WASHINGTON, U.S.A.

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In 1990, the U. S. Department of Energy's primary mission for the Hanford Site in south-central Washington shifted from the production of nuclear materials to environmental restoration. Environmental restoration of the Hanford Site involves characterization, cleanup, and isolation of radioactive and nonradioactive wastes generated in conjunction with production reactors, chemical separations and other activities related to the production and purification of nuclear materials on this 560-square-mile tract of semiarid land over the past 45 years. Over 1500 locations or units have been identified that may require characterization as part of state and federal environmental regulations.

One of the most important activities in these environmental efforts is the determination of the natural range of soil and groundwater background compositions to use as a baseline for defining contamination and cleanup levels, and in assessing risk. Geologic and geochemical data form the basis for these characterization efforts and also constitute the technical basis for a Sitewide approach to the characterization of soil and groundwater background at the Hanford Site.

The Sitewide approach has been recommended over the alternative approach of establishing backgrounds for each waste unit on the Hanford Site because (1) it provides more accurate and representative information on the natural range of soil and groundwater compositions, (2) environmental restoration of soil and groundwater are evaluated and performed on a scale that extends beyond the dimensions of individual units, and (3) all waste units share a common vadose zone sequence and groundwater in a single unconfined aquifer.

Geologic and geochemical data have been used to develop process models that aid in understanding and interpreting the nature and scale of compositional variability of soil and groundwater background compositions. It is indicated by these data that (1) the compositions of most vadose zone sediments can be considered as a single compositional series; and (2) the natural variation in the composition of groundwater in the unconfined aquifer and of the sediment in the vadose zone exists on the scale of the entire Hanford Site.

The key element of the soil background model is that the compositions of the vadose zone sediments are related by their common origin, sources, and mode of deposition associated with Pleistocene cataclysmic flooding. Lateral and vertical compositional variability is attributable to differences in the proportion of quartzofeldspathic and basaltic matrix components in the sediments, which are related to the manner in which the sediments were deposited during and between flooding episodes. Eolian deposits that locally veneer these sediments are also genetically and compositionally related to these glaciofluvial sediments.

The principal concepts in the groundwater background model are (1) groundwater composition in the unconfined aquifer is influenced by natural recharge, interaction with the underlying confined aquifers, and water-rock-air reactions; and (2) the groundwater compositions generally evolve along reaction paths that converge toward solubility-controlled concentration levels.

The Sitewide approach to soil and groundwater background characterization at the Hanford Site provides a consistent basis for evaluating contamination. It also improves efficiency in characterization activities, and remediation and restoration programs for ensuring protection of human health and the environment.

THE USE OF BIRCH SAP FOR GEOCHEMICAL MONITORING

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Many different types of materials have been utilized for geochemical and environmental studies. Among plants the birch has found widespread use as an indicator plant. However, very little has been written about the chemical composition of the bleeding sap of birch, especially about its use for geochemical and environmental monitoring. Harju and Hulden have in a recent paper[1] described the use of birch sap (mainly *Betula verrucosa*) as a tool for biogeochemical prospecting. Due to its common occurence in the northern hemisphere the birch is a very suitable indicator plant for environmental monitoring.

From analytical point of view the bleeding sap of birch is simple to sample and analyze. For instance when using DC plasma atomic emission spectrometry (DCP-AES) and graphite furnace atomic absorption spectrometry (GF-AAS), the sap can be analyzed directly, without time-consuming and thus expensive sample preparation steps. Several advanced analytical techniques were used in the present study. Major and minor elements were determined with DCP-AES. Trace element analusis were performed with GF-AAS. Ultra trace elements and the isotopic composition were determined by inductively coupled plasma mass spectrometry (ICP-MS). Conductivity and pH of sap samples were measured with conventional equipment.

Potassium, calcium, magnesium, manganese, phosphorus and zinc are the most abundant elements in birch sap. Their concentrations mostly exceed 1 mg/l. About 10 additional trace elements were analyzed. If one compares the mineral element concentration of birch sap with the corresponding concentrations in soil water, one can find that the birch has a very selective uptake of essential elements e. g. potasium, manganese, zinc and phosphorus. The sugar content of birch sap, 0.5 - 2 %, is low compared to that of the sugar maple.

The usefulness of birch sap for geochemical monitoring was tested by sampling around mineralisations or above bedrock of known composition. Clear anomalies could be observed at sampling intersects crossing mineralisations. However the contrasts for sap are smaller than for water samples taken from the same sampling sites . Thus a damping effect can be observed for instance on the heavy metal ion concentrations in birch sap. Also the daily and seasonal variations in bleeding and element composition of birch sap were studied A drawback when using birch sap as a sampling media is the realatively short bleeding season, 4 - 5 weeks in the Nordic countries.

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Field Validation of Conceptual Models of Mobilization and Transport of Volatile Petroleum Derivatives in the Unsaturated Zone.

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ABSTRACT

A conceptual model of the mobilization, transport, and fate of volatile petroleum hydrocarbons in the unsaturated zone is presented based on field data from long-term, interdisciplinary research begun in 1983 at the site of a crude oil spill near Bemidji, Minnesota. Oil floating on the water table is becoming denser, more viscous, and depleted in volatile and soluble constituents. The major features of the contaminant plume in the unsaturated zone can be explained by assigning each major chemical constituent to one of three groups based on their sources, transport paths, and fate: (1) C_3-C_8 alkanes, (2) benzene and alky-benzenes, and (3) methane. C_3-C_8 alkanes are the least complex group. They comprise about 85 percent of the contaminant mass, their source can be characterized by a single partitioning term, and their movement is not strongly coupled with ground-water flow because water/soil gas interchange is not a major factor. The benzene and alky-benzenes are of intermediate complexity. Their high aqueous solubility causes them to partition to and be transported with ground water. Consequently oil/gas, oil/water and gas/water partitioning, and concentrations in ground-water must be known. The most complex group consists in methane which is produced both in the unsaturated and saturated zone under anaerobic conditions. Therefore two biologic rates need to be specified which in turn depend upon substrate concentrations controlled by saturated- and unsaturated-zone processes.

PRESENTATION OF THE COVERED CATCHMENT PROJECT AT THE LAKE GÅRDSJÖN, SWEDEN.

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Some major questions about the future environment will be answered within the IVL's Roof-Project:

* How fast will the forest and forest soil recover ?
* Does reducing acid input to this forest lead to an improvement in the quality of runoff water ?
* Will the output of acidity and toxic ions such as aluminum be reduced and if so, by how much ? Will there be an initial deterioration in water quality, as predicted by some models ?
* Will the runoff water be suitable for fish if acid input from the atmosphere is reduced ?
* How fast will any improvement in water quality occur (year/decades) ?
* If existing acidification models does not fit the response of the catchment as in the experiment - is it possible to modify the models further ?
* Does a reduction of atmospheric mercury and cadmium input to a forest ecosystem lead to a reduction of mercury and cadmium output in soil- and groundwater ?

REDISTRIBUTION OF METALS FROM A CONTAMINATED DRAINAGE SYSTEM - PROCESSES IN THE SEDIMENTS OF AN ACIDIFIED LAKE

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Sediments in surface water systems (streams, lakes etc) are generally sinks for suspended particulate matter in the aqueous phase that eventually settles. Since the particles phase can act as efficient adsorbing carriers of trace components (organic substances as well as metals etc), these agents could also accumulate with time in sediment bottoms. Oxides/hydroxides of Fe, Al or Mn as well as quartz, clay minerals and organic aggregates are typical carrier substances. Processes within the sediments may lead to changes of the chemical specition of the trace components, mineralization, respension or dissolution etc. Thus, the sediments my serve as secondary sources of the various components that are accumulated, or enrichment processes could even increase the concentration in the solid sediment phase.

Processes in bottom sediments from a metal contaminated lake (Lake Gruvsjön, Bersbo, Sweden) are studied in detail in the present work. This lake has received large amounts of metals from a mine waste deposit in the vicinity. Three sediment cores from the lake were sampled and sliced into 1-2 cm thick sections. For each sektion the following analyses were performed:

i) Porewater analysis
Porewater was isolated by centrifugation. Colloidal particulate matter in the porewater phase was isolated by a sequential filtration technique as well as by photon correlation spectroscopy. All fractions were analysed with respect to pH, Al, Ca, Cd, Cu, Fe, Mg, Mn, Zn and TOC.

ii) Analysis of the solid sediment matrix
A sequential leaching procedure was followed for all sections in order to identify the nature of the trace element/sediment interaction (ion exchange, association to carbonates, hydroxides, organic matter, sulphides; in the residual solid phase etc). The same elements were determined as in the porewater analyses.

The trace element distribution versus depth is discussed in terms of chemical transformation and transport processes, and the role of the sediment as either "sink" or "source" for the accumulated trace elements is illustrated.

THE EFFECT OF CHEMICAL FACTORS ON OCCURRENCE OF ATYPICAL MYCOBACTERIA IN RIVER WATERS

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Atypical mycobacteria are acid-fast bacteria related to tuberculous bacilli. They are common saprophytes in all natural ecosystems and some species are, however, also pathogenic. In man pathogenic species may cause pulmonary disease similar to tuberculosis, lymph node and other soft tissue infections and in immunocompromised patients even fatal disseminated infections. Sources of these infections are considered to be in the environment. Insidence of atypical mycobacteria in clinical specimens turned to increase at the end of the 1970's (1,2). Some new pathogens, including a "Scandinavian-British" species Mycobacterium malmoense, were also found at the 70's (2,3). Geographic variation in the incidence of isolations from clinical samples and in infections caused by atypical mycobacteria (2,4) as well as in occurrence of atypical mycobacteria in the environment have been detected (5). Reasons to these phenomena are not known. The origin of newly detected species is also unknown. According to Kazda (6) low pH of water and according to Brooks et al. (5) low pH of soil supports occurrence of atypical mycobacteria. Based on these reports, it seems possible that acidification of the environment may partly explain observed increase in nontuberculous mycobacterial infections. However, ecology of atypical mycobacteria is poorly examined and more information about effects of pH and other chemical factors on the occurrence of mycobacteria is needed. In this study, relationship between the occurrence of atypical mycobacteria and chemical factors was examined in small rivers. Fifty three water samples were collected from small catchments in a linear belt crossing Finland at Vaasa altitude. According to a preliminary study of these waters a pH gradient in this belt exists: pH decreases from east to west (pH 7.0 - 3.8) (7). Mycobacteria were cultivated using a plate count technique. Cultures were incubated at 30 °C and 42 °C up to six months. Acid-fast colonies were isolated for identification by gas chromatography. Chemical parameters including pH, electric conductivity, $KMnO_4$ -value, dissolved O_2 and CO_2, HCO_3 -alkalinity, SO_4, NO_3, Cl, F, total C, total N, metals and temperature were determined at Geological Survey of Finland. These parameters were correlated to the occurrence of atypical mycobacteria.

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ENVIRONMENTAL MONITORING WITH RIVER SUSPENDED MATTER; A CASE STUDY IN RIVER DALÄLVEN, CENTRAL SWEDEN.

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The traditional techniques in monitoring programmes for heavy metals in rivers usually include analysis of dissolved element concentrations and sediment samples. The concentrations of several heavy metals in natural waters are, however, very low and there are problems with contamination and analyses. Sediment analyses are comparably less troublesome but it is difficult to take representative samples because of alterations during early diagenesis and the complicated sediment patterns in rivers.

Sampling and analysis of suspended matter is an alternative method ora complement to the traditional techniques.Suspended particles reveal the actual composition of the particulate phase prior to alterations during sedimentation, which makes comparisons between samples more reliable. In relation to the dissolved phase, suspended particles have higher contents of trace metals and show a higher signal to noise ratio.

In this study dissolved and suspended element concentrations are presented from River Dalälven, central Sweden. The river is contaminated by acid mine drainage and data from the most polluted tributary, Garpenbergsån, are also presented. A technique to calculate historical background concentrations of dissolved and suspended trace metal concentrations in river water with the help of the analyses of suspended matter is discussed.

Element/aluminium ratios in the suspended phase showed that Al, K, Mg, Ti, Ba, Co, V, Zr were present almost exclusively in detrital particles together with a large fraction of Si. The Al-normalized ratios for Mn and P, Ca resp. Fe were 5, 5, 3 and 2 times higher in suspended matter compared with river sediment. This indicates that 80%, 80%, 60% and 25% of the Mn and P, Ca resp. Fe contents were recirculated to the water column during early diagenesis in the sediment.

The sediment in River Dalälven is polluted by As, Cu, Hg, Pb, Zn and to some extent Cr and Ni. Arsenic, Cu, Hg and Cr showed an even stronger enrichment in the suspended phase indicating that 30 to 50 % of these elements are recirculated to the water column during early diagenesis. Zink was 10 resp. 50 times enriched in the suspended phase compared to the local bedrock. However, Zn showed similar concentrations in sediment and supended matter, suggesting that this element was not significantly mobilized during early diagenesis. Lead showed a lower concentration in the suspended phase compared with sediment, indicating a reduced anthropogenic input.

Large temporal variations of the dissolved and suspended Mn concentrations were observed in the river. During flood in spring approximately 70% of the Mn load was in the dissolved state. In early June, Mn started to change phase and in mid July more than 90% was in the suspended phase. Three minor peaks of dissolved Mn were correlated in time with lowered oxygen saturation and increased dissolved concentrations of Cu, Pb and Zn.

GEOTOXICOLOGY OF MULTIPLE SCLEROSIS: PROVINCE-WIDE CORRELATION OF WELL-WATER CHEMISTRY WITH CHILDHOOD HOMES AND INCIDENCE OF M.S. PATIENTS.

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The overall prevalence of Multiple Sclerosis (MS) in the Province of Saskatchewan exceeds 1 patient per thousand population. Besides this high background-frequency, this province has a documented hot-spot (cluster-focus) of MS at the hamlet of Henribourg, Sask., and a low-incidence area as well. Our previous research compared the geochemistry and well-water chemistry of Henribourg *versus* the low-incidence area, and suggested soil and water chemical differences that might be related to MS. Most of these involved trace elements, although some major and minor constituents appeared to associate with the MS cluster: calcareous soil; chloride rather than sulfate type water; and more nitrate or nitrite in the well water.

The present study seeks to determine which environmental chemical factors, identified as correlates of MS in hot-spots, may also correlate with this disease over a wider area. The geographic distribution of MS was determined over the entire Province of Saskatchewan (total population one million), but excluding centres using surface-water supplies. Two criteria were used: childhood home location (by manual search of M.S. Research Clinic and University Hospital records) and location at diagnosis (by authorized computer search of Saskatchewan Health Records). Well-water data for the same municipalities (obtained from historical well records) included elevation, depth, stratum in which the aquifer lay, and the major and minor constituent levels found in the water. MS frequencies *per capita*, both for farm and for non-farm locations, were tabulated separately, for each municipality. The well-water data were tabulated according to the same schema.

Among the major and minor constituents, only one had levels that were consistently and markedly higher in areas with higher frequencies of MS, whether in terms of childhood homes, or residence at diagnosis. This constituent was "nitrate plus nitrite."

The same constituent appeared also to be associated with at least two cluster-foci of MS, but it would be premature to conclude that nitrate or nitrite has any role in MS. The factors governing nitrate and nitrite distribution could also control the distribution of some other chemical that may be relevant to MS. Those controlling factors themselves may have a direct or indirect role. Alternatively, some totally unrelated, but relevant, factor may, by chance, have a similar geographic pattern. Soil types, for example, have a pattern grossly similar to those seen for MS or nitrate, across Saskatchewan. It should be emphasized that patients diagnosed as having MS according to the computerized records, still need to be verified by specialists in MS neurology.

Complementary studies include correlation of MS with trace element geochemical mapping in Saskatchewan (with Dr. Colin Dunn of the Geological Survey of Canada), and comparison of microgeography and geochemistry of MS cluster-foci, internationally.

THE GENESIS OF HIGH FLUORIDE GROUNDWATERS IN SOUTHERN INDIA

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Groundwaters excessively high in fluoride are common in India, especially i Rajasthan and in the interior of the Indian peninsula. More than half a million people are seriously affected by fluorosis.

Investigations on the genesis of this type of water have been carried out in Tamil Nadu, Coimbatore district and in Andhra Pradesh, in Nalgonda district. In Coimbatore up to 6 mg/l of fluoride have been found whereas in Nalgonda as much as 12 mg/l have been detected in this investigation. Both levels are high enough to cause skeletal fluorosis under the conditions present in villages concerning water intake and intake of nutrients. The areas are underlain by precambrian gneisses covered by generally rather coarse Alfisols. The high fluoride wells are found in restricted areas with slightly alkaline soils having a raised exchangeable sodium percentage(ESP). Locally the high fluoride wells are situated in the valley bottoms. The water chemistry indicates that CaF_2 is serving as a solubility control. The soil profiles carry an abundance of calcretes, especially near the valley bottoms where the calcrete may be found as beds several metres thick. The calcretes are calcitic in upslope positions but predominantly dolomitic near valley bottoms. The calcrete concretions are enriched in fluorine, as much as 10 000 mg/kg has been recorded. The dolomitic concretions have about 5-10 times as much fluorine as the calcitic ones. The soils in valley positions are slightly alkaline having ESP of more than 15 %.

The formation of high fluoride groundwaters is an effect of the high evapotranspiration in combination with the alkaline soil giving low concentrations of calcium in soil solutions. This in turn allows high concentrations of fluoride considering that CaF_2 acts as a solubility control. The original sources of the fluoride are the silicates especially hornblende and biotite. Although CaF_2 was not possible to detect by X-ray diffraction it is probably coprecipitated along with the carbonates especially the dolomite. Valley bottom positions should be avoided when drilling wells for drinking water purposes in areas with high fluoride groundwaters.

HEAVY METAL SPECIATION AND ITS BIOLOGICAL CONSEQUENCES IN LAKES POLLUTED BY SMELTER FALLOUT

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Comparative study of eight lakes polluted with Cd, Zn, and Cu from a smelter at Flin Flon, Canada showed that certain "bio-available" metal species have major effects on sedimentary micro-organisms, plankton, and fish, demonstrating that environmentally controlled metal speciation is of far greater biological importance than total metal abundance.

Methylation of Hg by sedimentary microbes was evidently inhibited by DTPA-extractable ("bio-available") Cd species in the sediments but did not show a significant, consistent relationship with the much more abundant DTPA-extractable Zn and Cu, or with total Cd, $CaCl_2$-extractable ("exchangeable") metals, or overall intensity of microbial activity as represented by CO_2 production. The bio-availability of Cd and other metals appeared to be depressed by sulfides but enhanced by organic matter. DTPA-extractable Cd interfered with the accumulation of Hg by northern pike, reflecting the fact that the Hg accumulated by fish at the upper end of the food chain is mostly in the form of methyl Hg. In contrast, the Hg content of white suckers, which are at a lower trophic level, was limited by sedimentary sulfides, possibly indicating that much of the Hg was inorganic owing to ingestion of benthic animals and sediment, Hg assimilation being hindered by strong Hg-sulfide bonding.

The effectiveness of DTPA-extractable metals in suppressing methyl Hg production increased in the order Cu < Zn < Cd, correlating positively with the ionic radius of the metal cation, the entropy of the metal oxide, and the solubility of the metal sulfide. The ionic radius effect suggests that the high toxicity of Cd compared with Zn and Cu resulted from especially strong covalent bonding of the metal by ligands at active sites of microbial enzymes owing to high cation polarisability, and the relationship with entropy suggests chelation; but the effect of sulfide solubility suggests that Cd, being less strongly bound than Zn and Cu by sedimentary sulfides, was more available to exert toxic effects on microbes.

As with Hg, the biological uptake of Cd, Zn, and Cu was mainly controlled by metal speciation in the sediments. Metal concentrations in > 10 μm plankton and the muscle, liver, and kidney tissues of fish increased with the abundance of DTPA- or $CaCl_2$-extractable metal species, or decreased with increasing abundance of metal-binding agents such as sulfides, Fe and Mn oxyhydroxides, and humic acids, but were generally independent of the total concentrations of the metals in the sediments. Again, pike and sucker gave contrasting results, probably owing to their different feeding habits.

EROSION POLLUTION OF AGROECOSYSTEMS BY BIOGENIC ELEMENTS

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The problem of protection and rational use of natural resources, including soils, is a major strategic direction in the balanced agricultural development.

A further growth of crop and farm animal production is impossible without maintaining and increasing the fertility of soils especially formed on slopes which account for more than a half of agricultural lands in this country. The crop yield decreases by IO to 60% or more and an enormous amount of humus and biogenic elements is lost on washed-out sloping soils.

Sizes of erosion biogenic nutrients losses vary greatly by zones depending on natural and anthropogenic factors.

The Non-Chernozem Zone loses yearly with soil wash-out from I ha of arable land average 30 to 227 kg humus, 3 to 2I kg nitrogen, 2 to 9 kg phosphorus and 24 to 88 kg potassium; the Chernozem Zone loses I39 to 343, 7 to I8, 4 zo IO and 44 to I09 kg respectively.

In addition, a significant amount of water-soluble nutrients is washed out from soil and applied fertilizers with a surface flow of thawing and storm waters. A nitrogen concentration in a liquid flow on fertilized fields in contrast to ones not fertilized increases I.5 to 2.7 times, phosphorus I.4 to I.7 times, and potassium I.4 to I.5 times as much. Most nitrogen and potassium is lost with water. Phosphorus losses are low, but its high concentration in the liquid flow is a main reason causing eutrophication of basins.

Erosion nutritive losses from fertilizers do not exceed I to 2%, yet when misusing fertilizer application technologies they can reach 20 to 50% from the rate applied.

It is estimated that the total damage from erosion losses of humus and biogenic elements in the country as a whole run to 7 to 8 billion roubles per year. Losses of biogenic elements on sloping lands cannot be practically prevented completely. The task is these losses should be brought to a minimum permissible level at which negative environmental impacts by biogenic elements must be

avoided. Investigations have shown that due to contouring-reclamation territorial management, location of soil-protecting crop rotations on slopes, use of antierosion soil treatments and environmentally safe fertilizer systems, sizes of biogenic elements losses in agroecosystems can be reduced I.5 to 2 times as much, i.e. to maximum permissible levels determined by the up-to-date state of soil-protecting crop farming in this country.

ELEMENTAL PROFILES OF SOME CYANOBACTERIA BY ICP-MS

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Environmental effects on living organisms is a complex function of the biogeochemical transport where many steps are unknown. The elements will be metabolised, retained or excreted and may give a different response before it ultimately reach animals and man. Acidification of the environment with an increasing release of elements and different compounds emphasizes the need of getting basic knowledge of normal distribution of elements in suitable bioindicators. The basic knowledge of normal values in different systems has been hampered by the lack of sensitive analytical methods. Recently the introduction of inductively coupled plasma mass spectrometry (ICP-MS) with multielemental capacity combined with high sensitivity and high speed has increased the possibility of examining more samples and several elements in a single analysis. Algae may be used for screening purposes because of their ability to accumulate elements. We believe that some algae may be used as a model to monitor metals from the environment. To explore this possibility we have used ICP-MS for estimating elements of cyanobacteria (blue-green algae) of which some are known to be toxic. We have also used ICP-MS for surveying of elements which may be of great help when looking for elements which may promote the growth of algae or potentiate the toxicity. Further details will be discussed in the paper.

BEHAVICRAL PROPERTIES OF TRACE METALS IN SOILS

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ABSTRACT

Soil-plant relationship is an important part of trace-metal cycling in the environment. The phytoavailability of metals control their supply to plants, and therefore their flux to food chain. The bioaccumulation of metals in surface soil horizons affect a temporal immobilization of metals and protects their transfer into hydrocycle.

The phytoavailability of metals is a function of several factors, of which geochemistry of the element, soil properties, and plant capability to metal uptake play a significant role. The speciation and localization of metals in soils are related to: (a) mineral forms inherited from parent material, (b) sorption and formation of complexes and minerals during soil processes, and (c) compounds at the time of anthropogenic impaction. Thus, behavior and phytoavailability of metals in soils differ upon their origin (lithogenic, pedogenic, anthropogenic). The binding mechanisms of trace metals in soils are manifold and vary with mechanical composition of soils, organic matter quality and quantity, soil reaction, and redox and drenage conditions.

An understanding of variable properties of trace metals is a key to the prediction of their fate in the soil, and may serve for a better adjustement of quidelines for threshold values for loading and concentrations of trace metals to local conditions, with respect to climatic, soil, and vegetation aspects.

LOCAL INPUTS VERSUS LONG RANGE TRANSPORT: SOURCE APPORTIONMENT OF ANTHROPOGENIC TRACE ELEMENTS IN LAKE SEDIMENTS USING THE RADIONUCLIDES ^{210}PB AND ^{137}CS

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Sediments of remote lakes in the Adirondack region of New York State (U.S.A.) have regionally characteristic (anthropogenic trace element/radionuclide) inventory ratios reflecting regionally uniform deposition of these pollutants, which have been transported from industrialized regions of North America. It stands to reason that the sediments of non remote lakes in this region receiving significant additional inputs of these trace elements from local sources should have (anthropogenic trace element/radionuclide) inventory ratios greater than those observed in remote lake sediment cores. We have collected sediment cores from several Adirondack lakes which support significant anthropogenic activities within their drainage basins. On the basis of a comparison of the observed (anthropogenic trace element/radionuclide) inventory ratios of these cores with the corresponding ratios observed in remote lakes of the region, we quantitatively assess the impact of local human activities on the Pb, Zn and Cd budgets of these lakes.

EXAMINATION OF THE RELATIONSHIP BETWEEN ^{137}CS DIFFUSIVITY AND THE CLAY MINEROLOGY OF LAKE SEDIMENTS

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Lake sediment core profiles of ^{137}Cs, a fission product injected into the atmosphere during the period of atmospheric nuclear weapons testing during the 1950's and 1960's, often bear little or no resemblance to the pattern expected from well documented records of global fallout of weapons test debris. Since the atmospheric input function of ^{137}Cs is well known, we can use the observed distortion of this signal in sediment cores to better understand the nature of the biological and physical processes controlling ^{137}Cs mobility in the sediment column. Using a standard advection-diffusion model with a Fickian parameterization of bioturbation, we estimate the biological and molecular diffusivities needed to fit observed ^{137}Cs profiles in sediment cores collected from various lakes throughout the United States. Kd values derived from model derived molecular diffusivities are compared to the clay minerology of the sediments in the different cores. Thus, the relationship between ^{137}Cs resolution and the geology of lake drainage basins is explored.

GEOGRAPHICAL DIFFERENCES IN ACIDIFICATION IN DEEP SOIL PROFILES AS MEASURED BY EXCHANGABLE CATION STATUS AND SULPHURIC ACID POTENTIAL.

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Twentyfive podsolized soil profiles where sampled, if possible, down to 2.6 m depth. The profile sites where selected along three diagonals across Sweden, one in the south, one in the middle and one in the north respectively. The diagonals extend from southwest to northeast.

Effective base saturation where used to determine the exchangable cation status. In the mineral soil horizons most sites showed low to moderate base saturation (<50%) within the top 100 cm of the profile. Profiles that differed occured only on sites with a low biomass production. Below 100 cm base saturation increased substantially with depth in the east and north of Sweden and was generally higher than 80% at 200 cm depth. Sites in the southwest and west of Sweden had a consistently low base saturation (<25%) throughout the profile.

Measurements of the sulphuric acid potential (SAP), defined as $2pH + pSO_4$, in connection with intrinsic equilibrium constants for sulphate adsorption on goethite and gibbsite where used to predict the degree of sulphate adsorption. Sites in the southwest and west of Sweden seemed to be saturated or supersaturated with respect to sulphate adsorption deep down the profile while sites in the east and north still had a large sulphate adsorption capacity.

The geographical differences in acidification where consistent with the pattern of deposition of acidifying substances. Deep acidification with low pH and base saturation only occured at sites where the soil where saturated with respect to sulphate adsorption.

LONG PERIOD EFFECT OF SO AND HEAVY METALS AIR POLLUTION ON THE PROPERTIES OF PODZOLIC SOILS

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This soil study was a part of complex investigation of spruce ecosystems located on different distance from "Severonickel" smeltery plant: spruce shrubby-green moss - 100 km (Site 1); spruce-green moss-shrubby - 36 km (Site 2); spruce-drass-shrubby - 20 km (Site 3); rare spruce-empetrum - 7 km (Site 4).

At each site, four or six pits were dug in main structural parts of ecosystems, designated on the basis of the vegetatation cover.

The preliminary investigations show, that the interaction of pollutants with forest soil has complicated character and flows on the background of deep changes in structure - functional organization of the ecosystems.

Accumulation of heavy metals by organic layer is one of the evident direct effects of long period air pollution on soil properties. Cu content in this horizon increas from 45 ppm (Site 1) to 1200 ppm (Site 4); Ni - from 38 ppm to 2400 ppm, respectively. However, during the ecosystem degradation the ability of the organic layer to accumulate the heavy metals is decreased. The additional field experiment shows that the content of both Cu and Ni may reach to 5000 ppm.

The study reveals the essential spatial variation of soil properties within the ecosystem. The soil properties under

main vegetation associations of spruce - green moss-shrubby ecosystem (Site 2) are differed by morphological features; by content and composition of humus and element content in organic layer; by forms of iron compounds in illuvial horizon and some others. But in spite of big differences (about 1 unit of pH) of atmospheric deposition pH values under spruce canopy and between trees, the differences in pH and exchangeable bases in organic layer under canopy and open site do not reveal.

The direct effect of long period acid atmospheric deposition caused by air pollution on physicochemical properties of soil also was not evident. The air pollution has more appreciable effect on these properties through the phytocenosis structural changes. So, the green moss destruction in main vegetation associations (Sites 2 and 3) are accomponied by increasing of pH and content of exchangeable bases in organic layer of these structural parts of ecosystems. These observations and the additional experiments allow us to suppose that green moss, as well as a tree canopy, acidify the atmospheric deposition before their penetration into organic layer of soil.

We connected the changes of Corg content in organic layer with the litterfall input dynamics during the destruction of ecosystem.

The air pollution from "Severonickel" has most drastic and dangerous effect on soil through the destruction of dominant species of vegetation followed by the development of erosion processes.

MECHANISMS AFFECTING TRANSLOCATION OF HEAVY METALS IN AQUATIC ENVIRONMENTS.

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Heavy metal content in aquatic plants, sediments and water samples in the shallow coastal area around Stockholm, Sweden are presented together with growth experiments on aquatic plants performed in polluted and unpolluted sediment, with different combintations of heavy metals.

The plant-available fraction of metals in unpolluted sediment decreased in the order Zn>Cu>Pb, and was highest in contaminated sediments. Low organic content in the sediment resulted in a proportionally higher uptake of heavy metals in aquatic plants compared to the total amount available in the sediment.

Uptake and translocation of heavy metal content is influenced both by the amount of organic material and the heavy metal content in the sediment. Zink for example affects the possibility of aquatic plants to take up and accumulate other metals. High levels of zink in the sediment decreases the metal uptake by aquatic plants and thereby reduces the toxic effects on the plant. Zink additions to the sediment increased, both the plant-available fraction and the total concentration of Cu in the sediment, but decreased the uptake of Cu by the plants. The opposite was found for zink when copper was added. On the other hand, the availability of lead in the sediment was not significantly influenced by the amounts of Cu and/or Zn in the sediment.

Effects of metal content, pH and redoxpotential in the sediment on the metal translocation is discussed. Finally, the role of aquatic plants in the translocation of heavy metals is compared to other mechanisms, e.g. bioturbation, resuspension and sedimentation, in the aquatic environment .

INFLUENCE OF AQUIFER CHEMISTRY ON THE TRANSPORT OF CHROMIUM AND SELENIUM IN GROUNDWATER

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Aquifer chemistry strongly influences reactivity and transport of many ionic solutes in groundwater. Both Cr(VI) and Se(VI) are weakly adsorbing anions whose adsorptivities depend strongly on pH and concentration of competing anions like sulfate. The reduced species Cr(III) and Se(IV) sorb extensively throughout the range of pH and dissolved salt concentrations commonly observed in groundwater.

We have studied the transport of Cr and Se using small-scale, natural-gradient tracer tests in a shallow, sand and gravel aquifer in Falmouth, Massachusetts, USA, where a plume of sewage-contaminated groundwater underlies a zone of pristine recharge water derived from precipitation. Flow velocities in the unconfined aquifer were 0.3 to 0.5 m/day. The recharge zone (RZ) was characterized by 250 micromolar (μM) dissolved oxygen (DO), pH 5.0, and less than 100 μM sulfate. The sewage-contaminated zone (SCZ) was characterized by DO concentrations below 1 μM, 5 μM Mn, denitrification, pH 6.2, and greater than 300 μM sulfate. Experiments were carried out at 3 sites where groundwater was withdrawn, tracers including Br^- (conservative tracer) Cr(VI) and Se(VI) were added, and the groundwater with tracers was reinjected. At the oxic site (site O), recharge water with tracers was reinjected into the RZ. At the suboxic site (site S), sewage-contaminated water with tracers was reinjected into the SCZ. At the mixed site (site M), recharge water with tracers was injected into the SCZ. Breakthrough curves were collected at various depths and distances down-gradient. At site O, both Se and Cr were significantly retarded due to adsorption of Se(VI) and Cr(VI) at the low pH and sulfate concentrations. At sites S and M, Cr was attenuated, as indicated by the decrease in area of the breakthrough curve relative to Br; Cr(VI) was the mobile form and was not significantly retarded. Attenuation was due to reduction to and irreversible sorption of Cr(III). Se was transported conservatively. Adsorption of Cr(VI) and Se(VI) was inhibited by the high pH and sulfate concentrations in the SCZ.

Laboratory studies showed that reduction occurred in aquifer material from both zones but was much more extensive in material from the SCZ. The rate of reduction increased with decreasing pH, increasing temperature in the range 10 to 55 °C, and was not affected by sterilization. The results indicate that the reduction was carried out without direct microbial mediation by an agent present at low concentration in the aquifer material.

OVER A DECADE OF RENAL STONE ANALYSIS AT THE UNIVERSITY OF NATAL, DURBAN.

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For over ten years, urinary calculi have been analysed at the University of Natal using X-ray diffractometry. This technique identifies crystalline phases for the physician, whose treatment will depend on which components have been distinguished.

The mineralogy of human calculi form three main groupings :

1. Calcium oxalates, including the monohydrate (Whewellite) and dihydrate (Weddellite) forms.

2. Phosphates : a) Calcium compounds such as Apatite and Brushite.
   b) Magnesium compounds such as Struvite and Newberyite

3. Uric acid , uric acid dihydrate and other urate salts.

The presence of uric acid (circa 10% of stones) suggests a biochemical problem commonly requiring treatment with Allopurinol.

Phosphates comprise about 10% of all stones. Apatite as a major constituent can indicate hyperparathyroidism; whereas struvite forms only in a basic medium in the presence of ammonia. This urinary condition arises whenever there is an infection. Usually, the patient is treated with an antibiotic.

Calcium oxalate calculi, the commonest type (79%) in this study, cannot be ascribed to any one condition. However, the probability of their formation can often be reduced by

(i) increasing the water intake (i.e. diluting the urine).
(ii) reducing those foodstuffs from which they can be derived.
(iii) increasing the concentration of magnesium in the urine by regular ingestion of Epsom Salts or Milk of Magnesia.

In the Durban area, the rate of occurrence of calculi is extremely high among Whites and Indians, being comparable with areas of high incidence in the world termed "stone belts". A possible explanation for this may be due to the "softness" of the drinking water. This will result in a very low magnesium content in the urine, which when combined with the high sugar

intake of the "average" dweller provides ideal circumstances for the formation of oxalate to cause a stone.

Interestingly, the incidence of struvite calculi is considerably lower than in Europe. It is unclear why this is so. It may suggest a lower rate of infection locally, or, more likely, that diagnosis occurs earlier and thus appropriate medication is prescribed sooner.

Over four thousand stones have been analysed in our laboratory alone, with a Whites to Indian ratio of 3 : 1. However, for every 100 stones from Whites, only 1 stone is presented by Blacks. Thus, the current rate of presentation of calculi by Negroes is incredibly small; a fact well documented at King Edward VIII and Baragwanath hospitals. Approximate rates of occurrence of calculi in the various population groups are :

WHITES	: 1 stone per 500 of the population
INDIANS	: 1 stone per 1500 of the population
BLACKS	: 1 stone per 50000 of the population

At present, it is unclear what causes these significant differences, although dietary factors are a strong possibility.

TRACE METALS MOBILITY IN SOIL AS AFFECTED BY SOME AGROCHEMICALS

BY

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ABSTRACT

Mobility of some trace metals namely Lead, Nickel, Chromium, Manganese and copper was studied in an illitic fine sandy loam soil using soil thin layer chromatography. The effects of substituted acetic acid and organo phosphorus pesticides and chemical fertilizers like urea, Ammonium phosphate, Ammonium sulphate and Murate of potash were observed in soil with or without soil organic matter (SOM).

It was found that the trace metal mobility follows the order.

$$Ni > Mn > Cr \gg Cu > Pb$$

An addition of fertilizers and substituted acetic acid herbicides to soil, significantly enhances the mobility while organophosphorus insecticides increase the mobility at their lower application and decrease at higher rate of application in all the cases. The results are discussed with the help of metal interactions with SOM and fertilizer /pesticides, and their solubility in water.

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THE IMPACT OF METAL MINING ON THE UPPER VISTULA FLOODPLAIN, SOUTHERN POLAND

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The region situated between upper Odra and upper Vistula river system, Southern Poland, is an area of historic and present day metal industry. Since medieval times, silver and lead ores have been mined and smelted. At the end of 18th century zinc mining was initiated which by 1860 accounted for 40% of the world total production.

Heavy metals associated with exploatation and processing of metal ores have migrated to the Vistula fluvial system. Transported as bed and suspended load, they have been deposited on floodplains and stored in alluvia.

Upstream of Cracow the upper Vistula Valley is 3-4 km wide and filled with gravelly or sandy alluvia capped by fine overbank deposits. The river channel has incised 2-4 m into these sediments over the last 100-150 years and near the channel has deposited a series of inset terraces. Before dyke construction, in the middle of the 19th century, the whole valley floor was inundated during major floods.

Examination of Zn, Pb and Cd concentration in vertically deposited sequences of alluvia varying age shows very clearly the impact of ore mining and smelting in headwater areas. In older (prehistorical) fine-grained sediments concentration of Zn varied from 120 to 190 mg kg^{-1}, Pb 10-40 mg kg^{-1} and Cd 1-10 mg kg^{-1}. In younger alluvia, deposited in the last 150-200 years, metal concentrations are highly veriable. In some horizons Zn concentrations reach 11500 mg kg^{-1}, Pb 1745 mg kg^{-1} and Cd 625 mg kg^{-1}. Zn concentrations in overbank sediment decline more rapidly down the upper Vistula Valley than those of Pb or Cd.

The 0.5-0.8 km wide interdike zone of the upper Vistula Valley forms a significant "store" of heavy metal contaminated fine grained alluvia. The long residence time of heavy metals in these alluvial soils and sediments (typically varying from 10^1 to 10^3 years) is known to result in long lasting effects upon the quality and stability of aquatic ecosystems even after sources of pollution are eliminated.

HUMIC SUBSTANCES IN LATVIAN WATERS, THEIR COMPOSITION AND GEOCHEMICAL ROLE.

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The organic substances in natural waters is one of the most principal components which plays a very important role in geochemical processes. First of all, the analysis of humic substances should be mentioned which has been underestimated up to now. The biological importance of humic substances in the ecosystems of water bodies has been stated concerning its amount and the amount of other water components in Latvian rivers and lakes. In general, the inland waters of Latvia are characterized by a high level of organic substances, especially humic acids. High concentrations of humic substances (HS) can be explained by a high degree of swamping and an intensive eutrophication of lakes. The highest concentration of HS is in swamp waters, eutrophic lakes and rivers,draining in such regions as Salaca. High concentrations of HS are also in some of the biggest rivers of Latvia - Daugava and Lielupe, but that can be explained by humification of municipal wastes and wastewaters and by washing out of humus from soil. The total runoff of organic substances in to a Baltic Sea and the Gulf of Riga can be estimated: organic carbon 500 - 600 *103 t/year, humic acids 20-25 *103 t/year, fulvic acids 160-230 *103 t/year, reducing

THE INFLUENCE OF URANIFEROUS BLACK SHALES ON THE COMPOSITION OF SOILS AND FOOD CROPS IN KOREA

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This paper examines the influences of naturally occurring uraniferous black shales on the growth and chemical composition of crop plants and possible implications to human health. Some of the potentially toxic elements of concern to man are present in naturally occurring rocks. Black shales in Korea may be natural geochemical sources of trace elements such as cadmium, molybdenum, selenium and uranium. Soils derived from these black shales tend to reflect their extreme geochemical composition.

Geochemical surveys have been undertaken within 23 river valleys in Korea underlain by black shales and oil shale. Sampling of rocks, soils and crop plants has been carried out along transect lines within each valley. Samples have been analysed for 25 elements by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Trace element concentrations in rocks, soils and plants in the uraniferous black shale areas are significantly different from those in the oil shale area. The factors influencing the relationships between trace element concentrations in rocks, soils and plants are assessed and their importance to human dietary intake discussed.

SENSITIVITY TO ACIDIFICATION OF SOILS AND WATERS IN FINNISH LAPLAND

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The research reveals relations between the acidification of lakes and the geochemical properties in mineral soils of the drainage basins. The sensitivity and the risk to acidification of soils and lakes have been demonstrated.

The data on monitoring water quality shows that the acidification in Lapland is a very serious problem. The development of the acidification of lakes and soils is not explained only by models of emissions of long range transport. The acidification of lakes depends on the sensitivity to acidification and as well on the amount and the quality of emissions. The sensitivity to acidification depends on the amount, quality and availability of mobile elements in mineral soils of the drainage basins.

A large scale research program is being carried out by the Geological Survey of Finland and the Water and Environmental District of Lapland. The soil geochemistry is based on the stream sediment data of the Nordkalott Project and the regional till geochemistry data of the Geological Survey of Finland. The monitoring of the acidification of lakes in Lapland has been carried out by the Water and Environmental District of Lapland. The lake inventory has been done on the fall over-turn time when more than 900 lakes have been sampled. The drainage basin of the river Lutto has been studied in more detail.

According to the preliminary results following conclusions can be drawn:

- the sensitivity to acidification of lakes strongly depends on the geochemical properties of the soils in the drainage basins.

- the drainage basins of the headwater and the through-flow lakes with the alkalinity of $\leq$ 0.05 meq/l have lack of base cations in the mineral soils

- the drainage basins of the headwater and the through-flow lakes with the alkalinity of $\geq$ 0.15 meq/l have a good buffer capacity in the mineral soils

- the alkalinity of the groundwater lakes have no distinct correlation to the base cation sum in mineral soils of their drainage basins

sugars and proteins 20-80 * 103 t/year. High concentrations of HS in Latvian waters explain their high complexing ability for heavy metals and toxic microelements, and the dominating forms of their migration and speciation. Our analyses of heavy metal speciation forms have shown, that in most river water up to 80% of lead, 70% of cooper and nickel and 65% of zinc are transported as complexes with humic substances (fulvic acids). On the other side, due to high content of HS the inner waters of Latvia have a high complexing capacity, that we have determined for lead ion. This analysis showed, that natural potential of binding of toxic metals is high and binding(complexing) sites in HS molecules are far from saturated.

From some water bodies humic substances were preparatively isolated, purified and ottained in a solid form after lyophilization. The HS have been characterized by IR, UV and fluorescence spectroscopy and elemental and functional analysis. These investigations as well as the analysis of molecular mass distribution show that HS differ rather essentially in their composition and characteristics and these differences are caused by their origin and formation conditions. The composition of these substances speaks about a direct effect of ecological and biological condition of the water body on their composition, molecular mass and complex formation with heavy metals. Also, it is possible to differentiate the humic substances from soil and those produced in waters. We have also analyzed the influence of humic substances on the biological properties of water ecosystems.

GEOCHEMICAL CONSEQUENCES OF SOIL AND WATER POLLUTION IN LATVIA.

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A growing environmental pollution in the recent years has resulted not only in ecological and medical, but also geochemical consequences. In particular, it concerns the changes in chemical composition of inland water and the levels of soil pollution in Latvia during some recent decades. To estimate these changes the interrelations among the ingredients of inland water can be used as the total amount of various substances drained into the Baltic and especially into the Gulf of Riga.

The performed investigations revealed basic changes in the composition of water of the main rivers. The total amount of organic substances, of biogenous elements as well as various salts discharged into the sea has been observed to be increasing. At the same time it should be marked that the bounds among various elements forming the natural geochemical background are also submitted to changes. The pollution levels in Latvian soils and waters have been evaluated.

DISTRIBUTION AND MIGRATION OF IODINE IN SOME LANDSCAPES OF THE RUSSIAN PLAIN

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The distribution of iodine in the main components (soil-forming rocks, soils, ground waters, vegetation, soil microorganisms) of some landscapes typical for the Russian plain (on glacial, fluvioglacial, ancient alluvial, loess-kind deposits, eluvo-deluvium of permian red-coloured sediments) has been studied, kinetic rodanide-nitrite method of iodine determination being used.

The distribution of iodine in rocks and soils proved to be dependent upon their origin, the concentration of organic matter and granulometric composition. It is noticably concentrated in humic and calcareous horizons. It seems to be for active iodine water migration that hydrophyte families and spesies accumulate this element rather than mesophyte ones. Soil microorganisms contribute to iodine mobilization showing increasing abilities of its accumulation in soils with lower concentrations.Intensive iodine migration in water soluable form and its accumulation at biogeochemical barrier show themselves in a rather high vertical and lateral contrast of its concentrations in soils of conjugated elementary landscapes. In all so-called polesje landscapes are the least provided with iodine, cases of endemic deseases cooresponding to iodine deficit among animals and people being well known (Vinogradov,1927,1957 et al).Nevertheless iodine concentration in soils and vegetation of superaquaeous landscapes are mainly within normal for grazing animals (threshold concentrations of Kovalsky, 1974) presenting ecologically comfortable localities within the deficit regions.

LANDSCAPE-GEOCHEMICAL FOUNDATION OF THE INVESTIGATIONS AND MAPPING OF THE CHERNOBYL RADIONUCLIDES' ENVIRONMENTAL MIGRATIC

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The Chernobyl accident was followed by the release of a considerable quantities of short- and long-living artificial radionuclides in various occurance forms (Israel et al, 1986), that were patchily distributed in natural and cultivated landscapes of different origin and types.

Their structure is believed to be important at the very first stage of contamination forming local peculiarities within the polluted areas. Subsequent researches showed different patterns of redistribution and migration of radionuclides at the contaminated regions due to not only the chemical properties of pollutants but also the natural peculiarities of the regions themselves, e.g. types of biocenoses, soils, water migration, erosion, resuspension (to some extent at the arable lands), landuse, etc. (All-Union conferences in Obninsk,1987,1990,Suzdal,1989, Gomel,1990, International Seminar in Luxembourg, 1990, etc.)

The spatial complex of these factors is taken into account in landscape-geochemical investigations.As far as such approach enables to expose and display spatial peculiarities of chemical elements migration in geosystems of different ranks with due regard to their scales (elementary, regional) it proves to be the most suitable for the prediction of long-living radionuclides migration in the invironment and food-chains. The peculiarity of landscape-geochemical mapping of the contaminated regions for prediction purposes is mainly for the contemporary migration processes to be taken into consideration, those being biological cycles , landuse type, solid and liquid run-off, water regime, etc. Therefore according to the project of the medium-scale landscape geochemical and radioecological mapping of the contaminated areas in the USSR (Khitrov, Korobova, Linnik,1991) landscape-geochemical maps should be presented in three modes: 1/ typological (to display the main types of geochemical landscapes and their internal structure); 2/ display of common features of chemical elements migration and accumulation , including typical geochemical ai biogeochemical barriers; 3/ display of distribution and migration patterns of radionuclides (caesium-137, strontium-90) in various landscape-geochemical systems within the contaminated regions based on landscape-geochemical , radiation maps and experimental data.The last map is considered to be basic for spatial prediction of radionuclides migration and further radioecological mapping.

THE EFFECT OF XENOBIOTICS ON THE OXIDATIVE COUPLING ACTIVITY OF SOIL.

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The studies were aimed to determine the effect of xenobiotics on the oxidative coupling activity of soil. The polycyclic aromatic hydrocarbons fluoranthene, anthracene and the herbicides: iloxan, starane, grasp, x-pand were used in the studies. The hydrocarbons were introduced into the brown soil polluted with industrial dust containing aromatic hydrocarbons and heavy metals. The soil was enriched with glucose, treated with fluoranthene or anthracene and placed into the pots for incubation. The herbicides were introduced into the loamy sand in the field experiments. The samples of the soils were extracted with the citrate buffer pH 6 and 2,6 dimethoxyphenol was added into the extracts. The substrate was oxidated to the dimer 3,3'-5,5' tetramethoxydiquinone. It was found that fluoranthene or anthracene increased the oxidative coupling activity of soil after one day of incubation, but after longer incubation time the soil activity decreased. The oxidative coupling activity of loamy sand treated with the herbicides increased after one week of incubation where as after 3-7 weeks of incubation the soil activity decreased, particularly in the soil treated with grasp or x-pand. There was no correlation between the number of soil microorganisms and the activity tested.

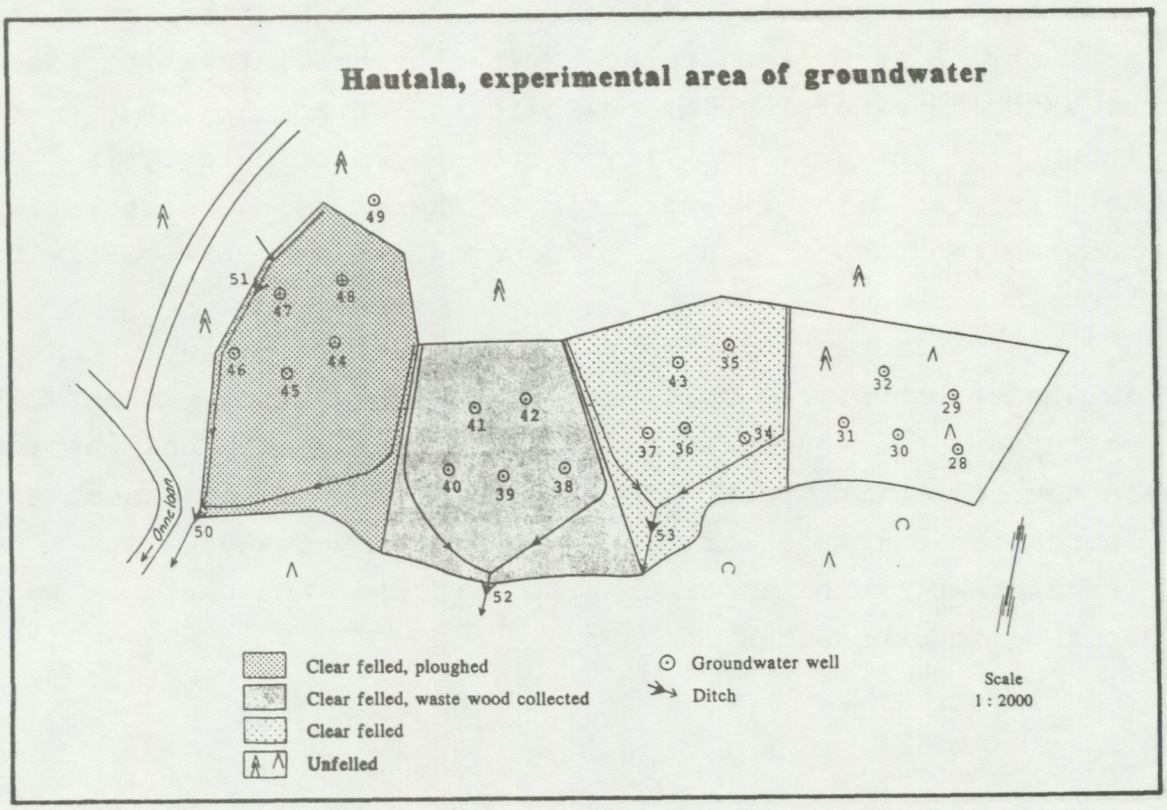
It could be concluded that the determination of the oxidative coupling soil activity showed the extent of pollution of the natural soil environment. Reactions running in the soil with part of microbial phenol oxidases and inorganic oxidants are of great importance in the transformation and incorporation of the xenobiotics into soil humic substances.

EFFECT OF CLEAR FELLING, WASTE WOOD COLLECTION AND SITE PREPARATION ON THE CHEMICAL CONTENT OF GROUNDWATER

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The research was commenced in 1978 by setting up two test plots, one in a fresh heath forest and the other in a slightly drier forest, with a combined area of about 10 ha and containing a total of 49 groundwater wells. This was followed by an 8 year calibration period up to 1986 during which fluctuations in the groundwater table were measured, and also the concentrations of nitrate and ammonium nitrogen, phosphorus, potassium, calcium, magnesium, iron, manganese and aluminium etc. in the groundwater each month from May to October in the last year before felling. The amounts of felling waste present were evaluated separately and the volume of timber felled taken from the harvesting statistics. Soil samples were taken at metre intervals from each groundwater well during excavation. The two plots were separated by a ditch to conduct the surface water away and water quality was also assessed in this ditch. The timber and felling waste was gathered up and the site prepared for reforestation in summer 1986, with one portion of each plot, comprising 10 groundwater wells in all, being left unfelled for comparison purposes.

Water quality results are available at present for the summer of felling and the following three summers. No appreciable changes are detectable in groundwater pH as a result of the above forestry measures, but a clear rise in nitrate concentration is observed, which, interestingly, is more pronounced in the plot from which the felling waste was gathered up than in that in which it was left in position. The concentration in the ploughed area was lower than in the absence of ploughing on one plot, where leaching occurred due to surface runoff, but correspondingly higher on the other, where no surface runoff occurred.



EFFECTS OF FUNGI ON TRACE ELEMENT SPECIATION - A CASE STUDY OF INTERACTIONS WITH IIb METALS AND PRODUCTION OF COMPLEXING METABOLITES

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Microbial processes can be important for the speciation and redistribution of trace elements in soil/water systems, both through direct interactions (adsorption, uptake) but also indirectly by effects on the chemical conditions on a micro scale. Interaction of IIb-elements (Zn, Cd, Hg) with three fungi (Trichoderma harzianum, Penicillium spinulosum and Morteriella isabellina) were studied in the present work.

The uptake of the three elements by the fungi was studied as a function of pH of the solution phase at constant ionic strength and environmental concentration levels of the metals by using radioactive tracers. The acidic complexing functional groups as well as the charge distribution on the outer surface of the fungi were studied by potentiometric titrations. Organic metal complexing metabolites that are excreted from the fungi were isolated and characterized (molecular weight and elemental composition).

The fungi generally exhibited large metal adsorbing capacities, which varied with the degree of fungal activity. Indications of hydrochemical effects related to the production of metabolites were evident. The importance of these phenomena for metal mobility and distribution in soil/water systems in general are discussed in the paper.

LEAD POLLUTION FROM MOTOR VEHICLE EMMISSIONS IN UASIN GISHU DISTRICT, KENYA

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A B S T R A C T

Motor vehicles in Kenya utilise leaded petrol, leaded gasohol (a blend of 10% power alcohol and 90% petrol) and diesel as sources of power. In the Uasin Gishu District, leaded gasohol and dieasel are used. The District is the granary of Kenya, producing 40% of its wheat, and a similar percentage of maize. Dairy farming is also prevalent. Due to the scarcity of arable land, it is common practice to see crop farming and livestock grazing taking place right upto the edge of roads and even highways. Lead levels were therefore determined in soils, wheat, maize and cow's milk from soils, crops and milk obtained close to the roads and compared to control samples away from the roads.

Lead levels decrease away from the road, with values as high as 3.05 ppm at the edge of the road, and as high as 1.36 ppm 80 m. away from the edge of the road. Wheat and maize cultivated near the road show lead levels of 0.11 - 0.18 ppm. Milk from cows that graze up to the edge of the road has lead levels of 0.14 ppm.

This study shows the need for legislation (a) to ban leaded petrol in Kenya and (b) to introduce laws on the minimum distance away from the road at which farming activities may be allowed to be practiced. The need for public education on the dangers of carrying out farming activities close to the road and/or living within 80 meters of a major public highway is also indicated.

GEOCHEMICAL MONITORING ON THE SEAFLOOR BY A TOWED GAMMA SONDE

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The seafloor is the ultimate reservoir for most of the anthropogenic interventions on land and in the atmosphere. Among geochemical species to be considered and monitored on the seafloor are natural (K, U, Th) and artificially (e.g., ^{137}Cs) occurring radioisotopes. Sometimes, to prevent cost-extensive solutions (e.g. detailed sampling) use can be made of the physical properties of the natural or anthropogenic accumulation. Among others, gamma radiation may be emitted by these species. Natural radiation measurements on the seafloor have been conducted for mainly mineral exploration purposes in the sixties and seventies by, e.g., Russian, American and British groups. Technology is now more advanced and makes it possible to investigate the application of geochemical tools directly on the ocean floor. Also, radiation field modelling can now easily be transferred to marine applications.

For continuously monitoring the radioactivity on the floor of the Danish sea territory a geochemical monitoring sonde has been constructed and tested. Being a prototype, construction strategies were based on the availability of components in an existing laboratory. The probe, which is mounted in a sled, is towed by a small research vessel along predefined survey lines. It consists of a water-tight encapsulated 6x4" NaI(Tl) scintillation crystal that via cable is connected to a 4-channel analyser. Data are generally collected via PC. A pressurized water-depth measuring device is coupled to the sonde to measure accurately the water depth, i.e. the distance of the sled above seafloor. At present, the sled can be applied to water depths of 40 m. Being designed for application

on smaller environmental research and monitoring vessels, the total weight of the sled is held at ca. 30 Kg.

A systematic towing along the island Anholt onboard M/S Gunnar Thorsson revealed anomalously high-radioactivity in sandy surface sediments, which probably can be ascribed to heavy mineral accumulations caused by the high-energy hydrographic regime around the island. Besides the mapping of heavy minerals the probe would be efficient in outlining naturally occurring phosphorite deposits, high- and very low potassium-bearing (quartz-rich) marine deposits, and radioactively polluted areas, including locally developed anoxic basins.

LANDSCAPE-GEOCHEMICAL INVESTIGATIONS OF THE BYELORUSSIAN TERRITORY CONCERNED WITH THE RADIONUCLIDE CONTAMINATION

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The Chernobyl accident was accompanied by a long-term emission of radionuclides into the environment. This emission occured in a synoptic situation favouring the creation of radioactive trails, which repeatedly overlaped some areas. The most important geochemical consequences of this accident within the Byelorussian territory involve: the primary differentiation of radionuclides in space and time due to the atmospheric transport and radioactive fallout; a very high level of the landscape contamination and a wide range of technogenic radionuclides; a mosaic pattern of the land pollution with radioactive anomalies of various intensities and composition; the second differentiation of radionuclides due to the modern geological and technogenic processes; the pollution of territories with peculiar landscape-geochemical features, e.g. Polessie landscapes with sandy soils favouring an active radionuclide migration; the formation of a new technogenic radionuclide geochemical province; changes of ecological conditions - endemic phenomena and the transformation of the geochemical environment; the global and permanent character of geochemical consequences of the accident.

Investigations involve field and stationary observations, which are carried out in the type landscape environments with due account for conjugate geochemical conditions and the main ways of the matter migration.

Strontium-90 and caesium-137 have been studied using multistage extracts, and the modes of their occurence were found to be different due to global (nuclear weapon tests) and regional (Chernobyl accident) fallout.

Landscapes and their constituents - natural waters, soils, recent river and lake sediments, vegetation show the redistribution of radionuclides tending to the decrease of the portion of short-lived radionuclides, the replacement of technogenic modes of radioisotope occurence by the natural ones, the matter redistribution according to general rules of the landscape-geochemical differentiation, the accumulation on geochemical barriers.

Radionuclides migrate and are accumulated in the water-soluble and adsorption forms, in the composition of the organic matter and hypergene minerals, as hardly decomposable natural and technogenic particles. The main sites of the radionuclide accumulation are concentrates of terrigenous minerals and particles; organogenous and argillaceous formations - silts and silt sheets, clays, sapropel, peat; humus and illuvial soil horizons; facies of a scroll meander, secondary pools of floodplains and oxbow lakes, terrace floodplain; geochemical barriers - groundwater discharge sites, iron and carbonate accumulations, deluvium trains and cones; some living organisms - plants and animals, etc. The river valley is a landscape barrier on the way of the radionuclide migration from the watershed territory.

LIGHT-WEIGHT DOUBLE PACKER EQUIPMENT FOR WATER SAMPLING AND HYDRAULIC MEASUREMENTS IN DEEP BOREHOLES

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The need to characterize deep and shallow ground water conditions in often remote crystalline terrains, both in Sweden and Finland, encouraged the development of a inexpensive, fast and easily transportable double packer sampler. The main aspects in the work were; 1) To combine water sampling and hydraulic measurement facilities within the same equipment. 2) Make the equipment fitting shallow and deep boreholes (1000 m) of various diameters (46-130 mm), 3) To be operated by a single person. In this paper we focus on the equipment configuration and on examples to conduct representative groundwater sampling and to measure geohydraulic parameters.

Some of the deep boreholes sampled earlier by a tube sampler, were reinvestigated by the double packer sampler. The significant differences encountered by the two sampling methods call for packer sampling technique in this particular case. It appears that the double packer technique is crucial for sampling representative water from fractures and to avoid mixing from borehole water. During pumping the slightly saline mixed water turned into a more saline water, with pH and electrical conductivity values representing the deep groundwater. In an other borehole the oxygen values in the borehole water were high. Meanwhile the pumped fracture water indicates appreciable lower oxygen values throughout the whole hole length. Uranium concentrations were also highest in the upper part of the borehole water and distinctly lower in the deeper parts of the borehole water. The same trend was encountered in the fracture water, however, dissolved uranium concentrations are less than one third of the values in the borehole water. To obtain representative groundwater samples a cleaning operation of shallow boreholes to remove the drilling contaminants and rock errtings was performed in combination with water sampling. Calculations revealed that in order to get a representative water sample, a volume five times as big as that below the packer should be extracted. Analyses of pH, Cl, Mg, Ca, HCO_3, Na, K and TOC in the removed water indicated stable conditions after the removal of the calculated water volume.

The main objectives of our hydraulic testing program with this equipment were: 1) To get an overview of the distribution of zones of different hydraulic properties. 2) To locate zones of high hydraulic conductivity for water sampling. 3) To estimate pressure differences between various conductive zones. 4) In some cases to measure the hydrological properties simultaneously with water sampling. This information is considered as a prerequisite for the evaluation and modelling of the prevailing groundwater situation and composition. Three methods are described the slug, the pumping, and the pressure recovery test.

GEOLOGY AND METALLOGENY: THE TWO MAIN FACTORS IN ENVIRONMENTAL GEOCHEMISTRY. CASE HISTORY OF THE SAINT-SALVY MINE (FRANCE)

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The Saint-Salvy Pb-Zn deposit is situated in the south of France, 70 km ENE of Toulouse. Located in carbonaceous black schists, underlain by sandy schists of Middle Cambrian age, the mineralization is essentially made up of galena (PbS) and blende (ZnS). The, heavily faulted, succession was later intruded by carboniferous granites. The Zn mineralization, 12% metal on average, occurs in lenticular bodies along a major fault, crosscutting a regional low-grade blende layer in black schists. Lead, 1% metal on average, occurs particularly in the major vein.

The deposit was discovered by a prospector in 1965 and the mining began in 1976; at the end of 1985, 2,000,000 m^3 of tailings were stored on the site. The tailings contain 1.5% Zn and 0.5% Pb, on average. A regional and local geochemical exploration (250 x 250 m soil grid) was carried out in 1971, before the mining phase; the area, including the mining site, was again prospected between 1978 and 1985 to find new targets (500 x 500 m soil grid).

The data from the exploration, before the mining began, show a strict relation between the Pb-content in soils and the surface trace of the major galena vein, with more than 900 mg/kg along 3 km. Zinc levels in soils, greater than 1,000 mg/kg, occur regularly over more than 4 km^2, in intimate relation with the associated black schists, mineralized in blende. Mineralogical and chemical studies demonstrated that galena from the major vein is the main Pb source in soils and that Zn came from blende dispersed in the black schists close to the vein, giving a reference level of regional dispersion.

The results of prospecting during mining operations gave a similar metal distribution in soils related to mineralization. The only difference with the "natural" state is the existence of a surface Zn halo around the tailings area, with a downslope extension of not more than 1 km, with levels from 500 to 1,000 mg/kg in soils.

The comparison of levels and extensions of natural metal distributions as compared to the pollution from mining, clearly points to the difficulty of discriminating between the two sources of metals. The corollary of this conclusion is the absolute necessity to take into account the actual influence of geological factors, the so-called "zero level", before the beginning of any mining or other industrial activities.

ORGANIC POLLUTION BY METAL-BASED INDUSTRY: THE PARADOX. THE PROBLEMATIC OF STANDARDS

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Usually, factories and other industries are located in valleys, along rivers, on alluvial deposits and close to the water-table. Normally, each plant uses raw materials and produces waste, the latter depending on the nature of the former.

To protect the environment, regulations and control checks take into account the specific nature of the raw materials and processes. For instance, the metal-based industry generally has to resolve the problem of one or a few metals only, but these can be present in very large quantities on the plant site (e.g., asbestos or cadmium). As soon as regulations and procedures are adapted to a specific plant, the industrial companies and authorities can manage the monitoring and the processing of the waste, and thus avoid environmental damage.

However, if the main sources of environmental contamination can be controlled, some experiences of general checks show that pollution sources can be numerous on a plant site and not only restricted to the raw materials directly in relation to the main processes. In most cases, such pollution comes from "common" products, daily used for plant operations, such as fuel, solvents and cleaners. In the metal-based industry such pollutants are used frequently, albeit in small quantities. Pollution is usually caused by small spillages, for instance when filling tanks; it is the cumulative effect of such spillages that causes the damaging effects of such pollution, for instance its slow infiltration into groundwater.

In France, regulations exist concerning the storage conditions for most of such products, even when they are used in small quantities. However, there is no obligation for industry to take samples for site control and to check for possible increases in background levels, thus anticipating the risk of pollution. Moreover, except for drinking water, no official standards exist for admissible concentrations in soils and water. In case of a general check-up of an industrial site, for instance when setting a plant, it is possible to refer to the guidelines in this matter of other countries, e.g., the Netherlands or Canada. Even so, such guidelines are usually unsuitable for highly industrialized regions, and the environmental experts are then obliged to consider the entire region as polluted.

EFFECTS OF pH AND ORGANIC MACROMOLECULES ON SIZE DISTRIBUTION AND SURFACE CHARGE OF COLLOIDAL OXIDES AND CLAYS

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Suspended solids in the colloidal size range are common in natural waters. This particulate phase would constitute a mobile solid phase which could act as an adsorbing carrier of e.g. trace metals in solution. The colloidal phase is generally composed of quartz, hydroxides and oxides of Al, Fe, Mn as well as clay minerals and organic macromolecular aggregates. Their surface properties are related to the composition of the aqueous phase (pH, Eh, salinity, presence of organics, etc).

Size distribution and surface charge of model substances (γ-Al_2O_3, Fe_2O_3, SiO_2 and kaolin) were studied as a function of the composition of the aqueous phase in the present study. Well-defined colloidal systems with a particle size in the range 50-500 nm were prepared. Ionic strength was varied within natural limits (0.001-0.7 M) by addition of $NaClO_4$, and the impact of specific cations and anions (Na^+, Ca^{2+}, ClO_4^- NO_3^-) was included as well as effects of pH (addition of NaOH or $HClO_4$). The size distribution was measured with Photon Correlation Spectroscopy (PCS). Scanning Electrode Microscope (SEM) was used to obtain information on surface properties etc (for estimation of surface area/volume ratios). The pH-dependent surface charge was determined by potentiometric titration.

Water composition (pH, ionic strength as well as the cation distribution) has a great impact on the size and stability of the particles. An increase in ionic strength gave a correspondingly increase in particle size. The fulvic acid stabilized the colloids but could also reduce particulate Fe(III) to soluble Fe(II). The observed influence of pH, salinity and organics on colloids is further discussed in the paper, particularly regarding the relevance for natural systems.

MANGANESE MINERALS AND ASSOCIATED FINE PARTICULATES IN THE PINAL CREEK STREAMBED, ARIZONA: A MINING-RELATED ACID DRAINAGE PROBLEM.

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The prime non-coal source of mining-related acid drainage in the United States is copper mining. Sixty-five percent of this mining is in Arizona. The Pinal Creek drainage basin in Arizona is a good illustration of pollution problems that can be caused by copper mining. Infiltration of drainage from copper mining and ore refining creates a ground-water acid plume, which seeps into the stream water and alters its composition. While passing through the alluvium, the acidified subsurface water reacts with calcite and, as the pH of the water increases, metals precipitate. As the alluvium buffering capacity is consumed, acid water moves downstream preceded by the water that has interacted with calcite. Iron oxides precipitate where the water is partially neutralized and, farther downstream well in advance of the acid front, manganese crusts develop where oxygen is present and the pH of the stream water is near neutral. These crusts are important because manganese and iron oxides exert a significant control on the distribution and concentration of trace metals in these and other natural waters.

In a recently formed black manganese oxide crust from the Pinal Creek streambed, manganese oxides were found precipitated on iron-enriched large particles (150- to 250-μ (micrometer)) and as fine particulates. The 75- to 0.1-μ particles were composed almost entirely of manganese oxides. Chemical analysis and X-ray diffraction (XRD) information suggest that the manganese solids in these fine particles were a mixture of $(Ca,Mn^{2+})Mn^{4+}_4O_9$-hydrate and $(Mn^{2+},Ca)Mn^{4+}_4O_9$-hydrate and possibly a small amount of calcian kutnahorite, a carbonate. XRD patterns of 75- to 0.1-μ particles from which manganese solids were removed indicated the presence of plagioclase, quartz, and lesser amounts of mica and chlorite. The manganese oxides obscured plagioclase and chlorite in these fine particles.

The possibility of a kutnahorite being formed was confirmed in the laboratory by XRD identification of that mineral among solids precipitated from aerated Pinal Creek water that had been maintained at mildly alkaline pH by slow continuous additions of dilute NaOH.

Knowledge of the chemical composition of the manganese crusts, the condition of their formation, and the mineralogy of their manganese oxides and associated minerals is a key to understanding the chemistry of this stream and can be helpful in many similar settings.

SOIL ACIDIFICATION AND BUFFERING PROPERTIES ON THE ION-BALANCE MONITORING PLOTS OF THE LAPLAND FOREST DECLINE PROJECT

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This work is being carried out as part of one of the subprojects of the Lapland Forest Decline Project, the aim of which is to determine the effects of industrial emissions (estimated to be around 600,000 tonnes/a) from the Kola Peninsula on the fertility, and acidification status and susceptibility of forest soils in Lapland. The results presented here concern the acidification status and buffering capacity of the surface soil on 7 of the 14 ion-balance plots established in Finnish Lapland. The material was collected during 1989-90.

All the plots have been established on dry mineral soil sites with tree stands dominated by Scots pine, and are situated along gradient lines running in a westerly direction from the major point emission sources in the Kola Peninsula. Considerable care has been taken in the field work in order to ensure that the site properties of all the plots are as similar as possible. This will assist in elucidating the effects of industrial emissions on soil properties and the whole forest ecosystem by minimising natural, between-plot variation along the lines.

Composite soil samples (20 samples/300 m^2) were collected from the O, A, B and C horizons down the soil profile. pH (in water and 1N KCl), potential cation exchange capacity (buffered NH_4OAc extraction, pH 7.0), effective cation exchange capacity (non-buffered $BaCl_2$ extraction) and base saturation (BSp, BSe) were used to quanitify the acidification status and buffering properties of the surface soil (0-45 cm). Base saturation depicts the proportion of cation exchange sites occupied by base cations.

The results are in good agreement with the vertical distributions typical of normal podzolic soil profiles. Soil pH increased along with increasing depth on all the plots. Base saturation was highest in the humus layer, but followed a similar trend to pH in the mineral soil. The lowest BS values were obtained, without exception, close to the interface between the A horizon and B horizon.

The pH and base saturation values are to a great extent determined by the distibution of fine material and organic matter down the soil profile. The results provide information about the progression of those soil processes

that have a very long time scale, such as the formation of a podzolic profile through natural acidification of the surface soil. It is very difficult to distinguish, on the basis of these parameters, between short-term changes caused by anthropogenic soil acidification and natural, long-term changes. Considering the rather low deposition values recorded in Finnish Lapland, it would appear that these soil acidification parameters primarily depict the situation that has developed under almost natural conditions.

AMBIENT pH AS A POTENTIAL CONFOUNDING FACTOR IN ENVIRONMENTAL MONITORING, EXAMPLIFIED BY THE AQUATIC MOSS, FONTINALIS ANTIPYRETICA.

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It is a well-known fact that metals are bioconcentrated by aquatic organisms to levels much higher than in surrounding water, and this is frequently used as an argument for their practice use as accumulator organisms in monitoring programs. Equally important, however, is the existence of a simple relationship between biotic and ambient level of metal.

The latter presupposes that the element is not homeostratically regulated by the organism; and, since homeostasis is most common in animals, plants may have a broader range of application as "general" indicators.

Even if a simple relationship ideally exists, this relation may easily be disrupted by local variations in pH, water hardness, humic content etc.; all of which are capable to modify bioavailability by effecting chemical speciation, or the permeability of biological membranes.

The effect of physico-chemical factors on net-uptake of metals was studied in situ by transplantation of the aquatic moss, Fontinalis antipyretica, along a fall-out gradient from the Rönnskär smelters. The study was provoced by a growing interest, in Sweden, for use of aquatic plants as accumulator organisms; being based on their simplicity in handling and analyses, high accessability, and high indicator value.

The attention is here focused at pH, as the probably strongest sole, modifying factor, having special relevance for Scandinavian countries with their wide-spread problems of acidification.

The results clearly show that small to moderate pH-depressions in the pH-interval 4.5-6.5 may strongly reduce the net-uptake of metals as Zn, Cd, Ni; thus confirming earlier experiences from laboratory-studies with aquatic plants.

The results are explained by a simple ionic-exchange model, where metal ions are replaced by hydrogen ions at the plant-surface.

The implications are obvious for interpretation of moss-metal-data from acidified waters; and may bear relevance for other accumulator organisms as well.

A NEW APPROACH TO ENVIRONMENTAL MAPPING: VISMAN'S THEORY.

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Visman's theory of bulk solids sampling has proven to be a powerful tool for the generation of geochemical maps. By means of a simple basic program it has been possible to relate a project budget to pre-established scientific objectives, such as:

- Degree of knowledge of the concentrations distribution.
- Precision of the estimate of the mean value for each homogeneous area in the map.

This tool is particularly useful in environmental mapping where knowing the precision of the estimate of the mean for every mapped unit is a basic requirement.

When applying this method a very simple previous study must be carried out, which yields some additional valuable information. The authors have made use of this approach to set the parameters for a map of airborne trace metals in Madrid, reaching the following conclusions:

- Optimum number and mass of sampling increments to achieve a well-balanced sampling regime (equal contribution of the different sampling stages to the final variance).
- Maximum size of the mapping unit so that a significant anomaly does not go undetected.
- Background levels and anomalies.
- Identification of three sources of pollution which account for more than 80% of the observed variance (urban traffic, heating and building construction).
- Simplified planning of the study of the whole city by means of an abacus which, given the unitary prices and efficiencies of personnel and equipment, relates visually: mass and number of sampling increments, variance of the estimate of the mean, mapping unit size and overall cost.

Session: 9. Impact of climatic changes on the geochemical environment.

STABILITY AND REACTIVITY OF SESQUIOXIDES IN CHANGING SOIL AND SEDIMENT ENVIRONMENT

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Oxides of iron, aluminium and manganese in soils and sediments are important adsorbents for heavy metals, oxyanions and acidic organic contaminants. In changing hydrological, thermal, chemical and/or organic matter regimes their solubility and surface reactivity will change. The effects are directly caused by changing redox potential, pH, temperature, concentration of complexing agents and ionic strength. The state of knowledge on these causes and effects is evaluated by review of recent literature. Reductive dissolution of oxides by decreasing redox potential, their enhanced dissolution by lowering pH and the role of organic and inorganic complexing agents are well documented, mainly by research on isolated oxides. For the total soil and sediment in the field where oxides coexist with other sorbents knowledge on oxide stability is poor. Also effects of changing pH, ionic strength and complexing agents on adsorption on oxides are extensively reported and described in models. Literature reveals very little on effect of temperature changes on stability and surface reactivity of oxides. Kinetics of the five types of cause/effect relations in field situations are poorly known.
Using this information European soil types on the scale of the FAO/Unesco World Soils Map are evaluated for their vulnerability for oxide dissolution and changing oxide surface reactivity. Criteria used are soil pH and base saturation, organic matter content, hydromorphic properties and texture. A number of thirteen soil units on this map is judged to be vulnerable in this respect. In addition some conclusions are drawn on coastal sediments. The results are applicable when local or regional soil pollution cases in Europe have to be assessed for release of pollutants under changing environmental conditions in future.

RADIONUCLIDES AND HEAVY METALS IN TOWN ENVIRONMENTS OF BYELORUSSIA

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Serious ecological situation in Byelorussia is connected with the acident of Chernobyl Atomic Power Station, rapid development of industry, transport, agriculture etc. in the last decades.

Radionuclide fallout on the territory of Byelorussian towns in the first days after 26 April 1986 was dependent on the air and rain mass movements. Maps of radioactivity are compiled for several towns located at different distances from Chernobyl. Dynamics of radionuclide decay and penetration into soil was studied. In cities the radionuclide fallout was found to be confined to regions with intensive technogenic dust emissions, as well as to river valleys, where the degasation of deep-seated zones through faults occurred side by side with the evaporation. Radionuclide wash out from upland territories and wind migration can be related to secondary processes.

Heavy metals were investigated in different parts of town landscapes: in soils, river bottom sediments, waters and plants inside towns and suburb area, where contamination may destroy the agriculture production.

The study of heavy metals in soils and their mode of occurrences give a possibility to make ecologic-geochemical mapping in several towns. For example, in Minsk four zones with a highly polluted soil (Pb, Zn, Cu, W, Mn, Cr, Ni, Hg, etc.) cover have been distinguished within the city territory. The concentration of heavy metals can be considered permissible only within 18.7% of the city area, moderately-dangerous - 41.7%, dangerous - 33.7% and extremely dangerous - within 59% of the territory, when the sick rate sharply increases.

The radioactivity together with heavy metals may have synergistic effect in causing illnesses.

THE FOLIAR CHEMICAL COMPOSITION OF SPRUCE (PICEA OBOVATA) IN BACKGROUND AREAS AND IN AREAS SUBJECTED TO INDUSTRIAL POLLUTION

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The transformation of the foliar chemical composition of spruce (Picea obovata) with increasing needle age and exposure to industrial pollution on the Kola Peninsula has been studied.

In the control spruce stand the total concentrations of chemical elements in current needles were lower than those in older needles ($p = 0.05$). The concentrations of chemical elements were in the following order for current needles:

K>N	Ca>P>Si>Mg	Mn>S>Al>Na	Fe>Zn	Cu>Ni>Co
$n10^4$	$n10^3$	$n10^2$	$n10^1$	$n10^0$ ppm

for older needles:

Ca>N	K>Si>Mg>P>Mn	S>Al=Na	Fe>Zn	Cu>Ni>Co
$n10^4$	$n10^3$	$n10^2$	$n10^1$	$n10^0$ ppm

Accumulation of elements such as Na and K were higher ($p = 0.05$) in current needles, whereas the Ca and Si concentrations were higher ($p = 0.05$) in older needles.

When exposed to industrial pollution by S, Ni and Cu, the total concentrations of mineral elements in the needles of all older year classes were lower than those in the control.
The enrichment of needles by pollutant elements was as follows: S - up to 2000 ppm, Cu and Ni - up to 50 - 100 ppm. A significant decrease in the concentrations of elements such as Ca, Mg and especially Mn for current and older needles was found. The tendency for decreasing K concentrations was marked only in current needles.

RECONSRUCTION OF WATER ACIDIFCATION IN A FORESTED CATCHMENT USING THE PROCESS-ORIENTED MODEL BEM

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Lange Bramke (LB) is a stream draining a 76 ha catchment in the western Harz Mountains (FRG). The area is covered with a Norway spruce forest (*Picea abies* Karst.). The residual layers in the LB valley are about 2.5 m in thickness. They are underlain by a Devonian sandstone which is almost impermeable. The soils are spodo-dystic cambisols. Since 1977, deposition rates, soil status, seepage water output in 80 cm depth and runoff from the valley have been investigated.

BEM (Batch Equilibrium Model) was developed and improved by J. Prenzel. Originally the adequacy of BEM was demonstrated by calibrating and applying it to consecutive batch experiments on the laboratory scale.
The basic common key processes incorporated include mass balance and equilibrium equations for cation exchange reactions, inorganic aluminium reactions, the carbonic acid - bicarbonate system.

In contrast to many other process-oriented models, the structure of BEM is not based upon a nonlinear sulfate adsorption process. The model includes reactions involving two solid phases of Al hydroxysulfate minerals: alunite and jurbanite. The underlying precipitation/dissolution equations are considered to be only model reactions for more complex processes of chemi-adsorption and/or solid formation, responsible for the SO_4^{2-} retention in soils and bedrock.

One method in calibrating the model on the catchment scale is to reconstruct past soil solution/streamwater chemistry. In the LB area the soils are extensively developed, implying a three compartment representation of the catchment: 1. layer, 0 to 80 cm (soils), 2. layer, 80 to 250 cm (bedrock), 3. stream (Lange Bramke). The soils or the bedrock are considered sufficiently homogenous. The model is implemented using average hydrologic conditions. Complex flow patterns (e.g. macropore flow) are neglected.

A 140-year deposition history, from 1848 to 1988, was estimated. The assumed long-term sequence of input changes in the LB area is based upon historic deposition records. For 1848 a SO_4-S load of 2 kg $\cdot$ ha^{-1} $\cdot$ yr^{-1} was chosen. The sulphur deposition in 1988 was assumed to be 45 kg $\cdot$ ha^{-1} $\cdot$ yr^{-1}.

Especially in the 2. layer the formation of alunite may control the SO_4^{2-} levels. The formed amounts are extreme sensitive to the availability of soluble Al. In the strongly acidified soil layer, the jurbanite precipitation increases at low pH levels (pH 4.2) and Al^{3+} values of about 60 µmol $\cdot$ l^{-1} . The results are based on the determination of different values for the activity product of $Al(OH)_3$ in the 1. and 2. layers, a relative high K^+ input through silicate weathering and a high K^+ discrimination at the exchange sites.

Hydro- and geochemistry in two catchments with different hydrological conditions.

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The hydrochemistry of groundwater and stream water depends on geochemistry and hydrological conditions within the catchment. Prevailing groundwater levels and flows of soil water are roled by geohydrology such as porosity, hydraulic conductivity, groundwater level and geochemical conditions. This poster presents results from investigations performed in two forested till catchments.

The investigations were based on field studies, in a humid climate, in hillslopes of two catchments with different geohydrological conditions. At locations of different soil types, the texture, porosity, hydraulic conductivity and soil water conditions, together with chemical composition at two to four soil depths were determined. Also runoff water composition was observed.

In one of the catchments with a fine-grained till also small amounts of added water rose the groundwater level to the upper soil layers. This was due to a stratified porosity and hydraulic conductivity that close to ground surface was comparably high, 10^{-5} $m*s^{-1}$. In levels of one meter depth the conductivity was about 10^{-7} $m*s^{-1}$. In downslope locations there was a stronger gradient in conductivity with depth than in upslope locations. Upslope predominated a vertical percolation and downslope an almost permanently high groundwater level was causing a considerable lateral groundwater flow there.

The chemical composition of the groundwater was influenced by the prevailing hydrological conditions. In the upper soil layers in downslope locations there were low pH-values, about 5.0, low content of base cations, 0.1-0.2 $meq*l^{-1}$ and an acidity of 0.02 $meq*l^{-1}$. In deeper soil layers, about 1.5 m, there were less acid conditions with pH 5.5, 0.3 meq base $ions*l^{-1}$ and a total alkalinity of 0.15 $meq*l^{-1}$. In upslope locations, there was a similar chemical pattern but more acidic.

At the other catchment with a coarse textured till, comparably high hydraulic conductivities, 10^{-5} - 10^{-4} $m*s^{-1}$, occurred throughout the whole soil profile. This influenced the groundwater level that often remained below a depth of two meters. This caused a similar chemical composition of the groundwater in different layers and also at different locations. The water was less acid as compared with the shallow groundwater in the fine-grained till and had a pH of 6.2, base cations totalled 0.3 $meq*l^{-1}$ and the total alkalinity amounted about 0.13 $meq*l^{-1}$.

SOIL SOLUTION CHEMISTRY IN A PODZOLIZED SOIL, WITH SPECIAL ATTENTION TO ALUMINIUM AND DISSOLVED ORGANICS.

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Soil solution chemistry was studied during four years in a podzolized glacifluvial sediment in a relatively unpolluted area in the north of Sweden, by percolation lysimeters installed under an undisturbed morlayer. The seasonal variation was greatest in the upper ten centimeters of the mineral soil. The concentration of dissolved organic carbon (DOC) was twice as high in autumn as in summer and the same was valid for aluminium and iron. The high concentration of these metals in autumn was due to complex formation with dissolved organics. About 75% of the monomeric aluminium was complexed by organics in the upper elluvial layer and about 45% in the upper illuvial layer. The concentration of calcium and magnesium in the upper ten centimeters was also much higher in the autumn.

Aluminium was speciated by ion exchange and weak organic acids were titrated and pKa determined. The concentrations of inorganic aluminium complexes were calculated. Complex formation constants for AlL (L organic ligand) have been evaluated as the best fit to data. For the autumn season, when the pH is lower, this constant was pK =4.76 ± 0.24 (n=8) and during spring and summer season, when the pH is higher, pK= 5.42 ± 0.31 (n=10). The correlation of weak acid to organic carbon was

weak acid (ueq/l) = 4.2 DOC (mg/l) + 18 (n=22; r=0.97).

The anion charge deficit was shown to be mainly due to dissociated weak acid groups.

The equilibrium of inorganic aluminium is also discussed in relation to solid phases. In deeper soil where the concentration of Al^{3+} is low and pH is high, the concentration of Al^{3+} is close to the equilibrium condition for microcrystalline gibbsite.

Soil solution chemistry in ordinary percolation lysimeters, where the roots have been cut off, were compared with the lysimeters that we used. The concentrations of major cations, anions and DOC were 1.5-3.8 times higher in the ordinary ones, probably caused by the root cut off.

ACCUMULATION AND TRANSLOCATION OF COPPER, LEAD, ZINC, AND CADMIUM AT 3 FOREST SITES ADJACENT TO THE CITY OF HAMBURG

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The general acceptation of existing damages in forests, especially in Europe and Northern America, has led to an intensification in research on elemental balance of forest ecosystems.
The results are shown in numerous comprehensive publications. In 1981 the project "Environmental control through investigation into forest ecosystems" was initiated by the "Umweltbehörde Hamburg, Landesforstverwaltung".
This project, first implemented by the team of Prof. Ulrich, to whom we owe many impulses in ecosystem analysis, was taken over by the Soil Science Institute of Hamburg in 1984.
The aim of this long-term study is the monitoring of in- and output of airborne substances (main nutrients, heavy metals, anions) in forests in Hamburg and the effect these elements have on to the ecosystem.
Beside the description of the sites, the balance of Pb, Cu, Zn and Cd in the forest stands and in the soils will be presented in this speech.
While the output of copper at all three sites (2 deciduous forests, 1 conferous forest) is always lower than the input, the balance of zinc and cadmium show annual and substrate - depending differences not only in translocation but also in desorption.
Lead shows atypical behaviour. At 2 sites, the input exceeds the output by 3 - 5 times during 1982 - 1989, resulting in remarkable accumulation in humus and topsoil (A_h). The reverse was detected at the third site 1983 and 1986, although at this place the percentage of loam is highest. After a phase of accumulation, there seems to be a limited desorption of Pb.
Whereas Pb- and Cd-contents are decreasing in canopy-

throughfall, stemflow, and precipitation in the open they increase in the biomass and in the seepage water. They exceed the values of the german drinking water decree (Pb = 40 ppb, Cd = 5 ppb) in the average 3 to 4 times, in the maximum up to 25 times.

The inputs of heavy metals are higher in the southern sites of Hamburg, depending on the closer neighbourhood of industrial complexes and the meteorological situation, than in the northern parts. On the other hand they accumulated better in the north because the soils here are more tenacious. The lower heavy metals reserves in the sandy soils of the south indicate, that there must have been a continous relative high output during the last decades, whereas in the north the output increases now, depending on the progessive acidification of the soils.

One can expect not only an accumulation, but also a mobilization of lead, cadmium and zinc at the three investigated forest ecosystems in the next years and decades.

DISTRIBUTION PATTERNS OF HEAVY METALS IN THE SOILS OF HAMBURG AND CALCULATION OF 100-YEARS-EMISSION

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The geochemical background of heavy metals in the soils and sediments of the Elbe river valley has been investigated in three cross-sections by drillings down to 8 m. By using the background levels the enrichment of heavy metals in agricultural soils not far off an industrial area in the southeast of Hamburg have been estimated. Referring to these works the investigations were extened to the whole territory of Hamburg.

In surface samples (0-5 cm) and selected profiles (27) the heavy metal content is examined. After the analysis of the first chance samples it turned out to be necessary to divide the town area into three parts of different density of sampling (500 m -, 1000 m - and 2000 m - screen).

The elements lead, arsenic, copper, zinc, and with modifications, cadmium, show the highest concentrations. The Hg-contents are altogether lower than assumed before. The contamination with chromium and nickel is to be neglected.

The frequency of contamination is shown by 5 classes (from "not" to "extremely" contaminated). The classes have been established according to the background levels and the available official guidelines.

High surface covering contamination is found near heavy metals manufacturing industries, especially in the southeast of Hamburg (Vier- und Marschlande). Since about 100 years the biggest copper smelting plant of Europe is established here with high emissions of arsenic and several heavy metals.

The close correlation between the Pb-, Cu-, Zn-, and As-content as well as the concentration of these elements in

some parks, which is sometimes very high, suggests that in several areas of Hamburg excavated material and waste products from industrial plants, coal power stations, and incinerating plants have considerably promoted the contamination with heavy metals. The results of the analysis of profile samples underline this assumption.

Very high concentrations are also found in upland landfills of dredged harbor mud. The extreme Pb-content in the soils is mainly due to road traffic, yet in some areas to industrial emissions as well.

An own created GIS computer programm enables us to calculate chorograms of the analysed elements.

Special interest was given to the vicinity of the copper plant and the agriculture (grass, arable land, vegetable farming). By the help of the computer model and several assumptions (soil density, translocation, only regarding samples from grassland, deduction of the natural content) the emissions of the last 100 years in this area (190 km^2) was calculated basing on the soil contents.

The total enrichments by airborne industrial immissions amount as follows (in metric tons): Zn = 8400, Pb = 3400, Cu = 2900, As = 750, Cd = 50, Cr = 20.

The investigations have started new dicussions on critical values of heavy metals in soils, especially on the different regional administration levels. They have also supplied the foundation for following investigations in highly contaminated areas.

GLOBAL POLLUTION RECORDED IN TWO GLACIERS OF THE ANDES AND SPITSBERGEN

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Dusts and gases introduced into the atmosphere by natural processes (geological and cosmic), as well as by activities of man can be deposited and "stored" in glacial ice. In areas where horizontal movement of the glacier is insignificant or non-existent the annual glacier-ice layers are formed. In this way, records are obtained on the atmospheric components and their variations in time.

Glacier-ice samples were collected from the Broggi glacier in the Peruvian Andes and from the Skilrygg glacier on West Spitsbergen. In the Broggi glacier, situated in the Cordillera Blanca range, a glacier crevasse lying at an altitude of 4766m was selected for sampling. 14 annual ice layers representing accumulation in the years 1961-1974 were taken. In the Skilrygg glacier which is situated 10 km north from mouth of Hornsund a glacier crevasse lying in accumulation zone at an altitude of 656 m was sampled. There were taken 27 annual ice layers representing accumulation in the years 1957-1983. Grain size, morphology, mineral and chemical composition were determined on dust separated from annual glacier-ice layers.

A maximum dust fall on the Broggi glacier has been approximately estimated at 0.2 t/km^2/year. The most abundant (about 70%) are grains 4-6 um in size. According to the classification of atmospheric dust the glacial material has been found to contain three types and five varieties of dust: natural dusts (terrestrial and cosmic), artificial dusts (industrial and originating from circum-terrestrial zones) and mixed dusts (products of photochemical reactions in the atmosphere). Natural dusts, blown away and transported by wind from the glaciated area, predominate. A few spherules of cosmic origin have been detected with optical and scanning microscopes. Artificial dusts of industrial origin have been found in all the samples. They form spheroidal glass bodies (product of combustion of coal) or aggregates of iron oxides and hydroxides (product of metallurgic processes). As water-soluble components sulfates and carbonates were identified (products of dust-gaseous photochemical reactions). Small metallic titanium spherules were also found in the dusts separated from the Broggi glacier. This material forms as a result of burning and melting of heat (titanium) shields of space rockets (or their fragments) when they enter the earth's atmosphere. An increased content of such spherules was noted in the ice of 1965-1970, that is, in the period of great intensification of flights to the Moon. It is the first report of titanium dusts of such origin found on the earth's surface.

SURVEY OF TRACE METALS IN HEADWATER LAKES IN FINLAND

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Water samples for trace metal analysis were collected from over 250 lakes included in the Finnish lake acidification survey conducted in autumn 1987. The objective of the selection was to cover the whole country, with the emphasis on headwater lakes in the most acidified and acid-sensitive (but relatively unaffected) areas. Mean area of the lakes was 38 hectares.

Samples were taken directly in acid-washed, HDPE bottles sealed in double plastic bags during transportation. Flameless AAS was used for the determination of Cd, Cu, Pb and Ni, and flame AAS for Zn. The lake water data was compared with catchment characteristics, regional metal concentrations in mosses and snow, as well as till geochemistry (fine fraction, partial dissolution in aqua regia).

The general water quality of the lakes was close to the average for small Finnish lakes. The heavy metal concentrations were similar to those reported in Central and Northern Sweden in recent years. The concentrations of Zn, Cd and Ni in water decreased on moving northwards, and reflects the pattern of atmospheric deposition as determined by the snowpack chemistry. Comparison of lake water chemistry data with the Scandinavian survey of metal concentrations in moss revealed that the average concentrations of Cd, Cu, Pb, Zn and Ni in water were all higher, the higher the regional concentration of the same metal in moss.

Acidic conditions were associated with high concentrations of metals in water. The strongest relationship was between pH and Al, but the correlations were also high for Zn, Pb and Cd. This was more pronounced in the southern areas. The concentration of Cu was more dependent on humus content of the water (total organic carbon, TOC) than that of Pb, Zn and Cd. The concentration of the land-derived metals Al, Mn and Fe were even more dependent on TOC, but on acidity as well. These relationships were similar to, but more significant than those reported in previous studies in Scandinavia. Concentrations of Zn and Cd correlated positively with the proportion of exposed bedrock, and Pb with the proportion of peatlands in the catchment.

A comparison of lake data with geochemical data of trace metal concentrations in till (Geochemical Atlas, Geological Survey of Finland) is in preparation and will be discussed. Lake water and till material showed eg. high Ni and Cu concentrations in some overlapping areas.

THE GEOCHEMICAL SURVEY OF TOPSOILS IN ENGLAND AND WALES

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Abstract

A programme which involved the chemical analysis of the 'total' concentrations of 16 elements in 6000 topsoil samples from England and Wales has recently been completed. The sampling strategy was unbiased, and samples were taken on intersections of a 5 km grid over the whole country. Elements determined were: Al, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, P, K, Sr and Zn. Amounts of trace elements extracted by EDTA have also been measured. This database gives unique information about the chemical status of the productive surface layer of the lithosphere.

Use of Tukey's approach of Exploratory Data Analysis, without the need for any assumptions about the statistical distribution of the data, has revealed the influence that geology and soil-forming processes have upon the elemental content of soils. This is exemplified in the Table below.

Another aim of the programme was to distinguish those soils with background, and unusually large or small concentrations of trace elements. One key finding was the great extent of Pb contamination in upland peats of the Pennines, Lake District and Wales, and a strong relationship between Pb and the organic carbon content of soils. Much of this can be explained by modelling using current and historical deposition rates of Pb from the atmosphere, and is thought to be due to fallout of Pb from mining, smelting and automotive emissions. However, other metals such as Zn and Cu are not enriched in peat soils.

The database is not only of value in delineating potential toxicity, but also to define areas of potential deficiency. An example is Zn, smallest concentrations of which occur in sandy-textured soils in specific areas of the country. Little work has been done on Zn deficiency in crops in the UK, but these data can be used to predict where it is likely to occur in future in sensitive crops. Workers in Eire have suggested that Zn deficiency in plants is likely when EDTA-extractable Zn is < 2 mg kg^{-1} soil. Applying this limit to the data set shows that 20% of soils are below this threshold value.

Applying similar established threshold values used in the UK for diagnosis of potential effects shows that 20% of soils are below 2.5 mg Cu kg^{-1}, where slight deficiencies of Cu are possible and 10% below 1.5 mg kg^{-1}, where deficiency is likely. Also, about 18% of soils contain less than 3 mg kg^{-1} Co, a situation which is likely to result in Co deficiency in ruminant animals. The type of soils associated with potential deficiency and their geographical spread will be demonstrated using full colour maps of the results.

A further use of the data is for environmental protection purposes. Toxic metals accumulate in soils due to, for example, application of wastes such as sewage sludge and domestic wastes, and fallout from the atmosphere. The excellent background values that can be derived from the data sets are valuable in formulating improved guidelines to set limits to the permitted inputs from such sources. However, the concentrations of some metals, an example being Cd, depend on the soil type (see Table). The influence of this finding on the type of limits to be set will be discussed.

Cadmium concentrations in topsoils of England and Wales (0-15 cm), summarised by soil texture. Data from McGrath and Loveland (1991).

Soil Texture	Total Cadmium (mg kg^{-1} dry soil)					
	No. of Samples	Minimum	25th percentile	50th* percentile	75th percentile	Maximum
Clayey	479	<0.2	0.8	1.0	1.3	19.2
Fine Loamy	2002	<0.2	0.6	0.8	1.0	40.9
Fine Silty	1063	<0.2	0.7	0.9	1.2	17.8
Coarse Silty	184	<0.2	0.5	0.7	1.0	3.8
Coarse Loamy	1143	<0.2	0.3	0.5	0.7	10.5
Sandy	229	<0.2	<0.2	<0.2	0.2	3.7
Peaty	557	<0.2	0.3	0.6	0.8	5.8
All soils	5692	<0.2	0.5	0.7	1.0	40.9

* Median

Reference

McGrath, S.P. and Loveland, P.J. (1991) *The Soil Geochemical Atlas of England and Wales*, Blackie, Glasgow

THE INTERDEPENDENCE OF SOIL AND WATER CHEMISTRY ON A CATCHMENT SCALE

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The neutralizing effect of soil-water interactions has been evaluated in a comparative study of three small forested catchments (0.5-1.8 km^2). Due to different geographical location in Sweden the catchments receive a varying load of acid deposition. Buskbäcken in the Kloten area in Central Sweden receive the highest amount of acidifying substances, Stubbetorp on the Southern Eastcoast slightly less and in Svartberget near Vindeln in the North the acid deposition is comparatively low. In Buskbäcken has the large acid deposition resulted in acid streamwater and a positive alkalinity can be measured only at periods of low flow. In Stubbetorp the streamwater still contains a small amount of alkalinity although the acid deposition is quite high. In the northern area, Svartberget, the acid deposition is low but the streamwater is acid due to a large content of organic acids.

The geological features of the three areas are similar. The areas are dominated by till soils mainly derived from granites and gneisses; the elemental composition of fine soil from the C-horizon however shows that the content of base cations differs, being highest in Svartberget and lowest in Stubbetorp. The hydrological conditions in the three areas are also quite different. The deep till soil in Buskbäcken is of a low permeability giving a more shallow drainage than in the other catchments. In the north the accumulation of snow gives rise to large runoffs in spring while especially in Stubbetorp melting of the snow during mild periods in the winter gives a less intense spring runoff.

In all the studied areas the pH is negatively correlated to runoff. In Svartberget this is coupled to outflow of organic acids but in the other areas sulphate is the dominating anion. A survey of the soil chemistry shows that the base saturation of the groundwater recharge areas is approximately equal in the catchments. The base saturation shows an increasing gradient from the groundwater recharge areas to the groundwater discharge areas. While this gradient was found in all three areas it was most pronounced in Stubbetorp, where the high base saturation in areas close to the stream stabilizes the pH on a high level despite the rather high rate of acid deposition and a poor mineralogy. The base saturation of the discharge areas is attributed to the outflow of groundwater relatively rich in base cations. Due to a low weathering rate and shallow runoff the exchangeable stores of base cations in the Buskbäcken discharge area are depleted giving an acid runoff.

A check on the element budget for the base cations show that the net result of the internal processes in the catchments (nutrient uptake/release, weathering and ion-exchange) is very similar in the three areas. The low rate of weathering in the hydrologically active zone in Buskbäcken is partly compensated by a relatively low nutrient uptake.

URANIUM SERIES DISEQUILIBRIA IN THE SEDIMENT-HOSTED URANIUM DEPOSIT OF COUTRAS, FRANCE: GEOCHEMICAL ASPECTS OF RADWASTE DISPOSAL

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Recent mobility of ^{238}U series has been investigated in the Coutras deposit (Gironde, France) located in Lutetian sandy and clayey sediments near the surface. Coutras could represent a good example of a radwaste repository site brought near the surface and accessible to meteoric waters, after a dramatic geological event. The Coutras deposit comprises a belt of tabular ore bodies separated in two areas by the Dronne River: the Jean Vincent area, close to the surface and the Le Fieu area located at a maximum depth of 100 m. Thorium content of whole rock does not vary significantly with U content. The hydrological regime in the Jean Vincent area is characterized by oxidizing waters flowing toward the Dronne River. Activity ratios (AR) of $^{230}Th/^{238}U$ in rocks range from 0.55 to 12 which demonstrate recent U accumulation and leaching. The $^{234}U/^{238}U$ AR range from 0.95 to 1.37 in rocks and from 0.94 to 1.16 in waters. The $^{234}Pa/^{214}Bi$ AR, obtained by gamma ray probing range from 0 to 45 which indicates extensive remobilization of uranium. However, the whole data indicate that leaching and accumulation of uranium are balanced. Recent accumulation of uranium is favored along redox barriers where Mo, V, Se, and As are also deposited. Uranium in mineralized black clay layers from the Jean Vincent oxidizing area is mobilized along bleached zones of a few decimeters thick but reaccumulates along redox fronts. Organic matter is destroyed in bleached clays but is extremely efficient in fixing uranium in black clays. Uranium in organic matter is mainly fixed as strong uranyl-organic complexes which transform into uraninite when heated in laboratory. Waters in the Le Fieu area are nearly stagnant, reduced and exhibit a different chemical composition than waters in the Jean Vincent area with higher content of major cations and anions, higher $^{234}U/^{238}U$ AR (1.33 to 4.63), radium and lower U content. The Le Fieu rock samples do not show any recent leaching of uranium but excess and deficit of ^{234}U are observed. Preferencial mobility of ^{234}U in the reduced Le Fieu area is interpreted by the recoil model. The results indicate that the radionuclides are mainly reaccumulated near the leached zones despite of the high mobility of ^{238}U and many of its daughter products.

LEAD DUST CONTAMINATED COMMUNITIES OF UNITED STATES CITIES.

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This study presents a lead dust contaminated community paradigm that, in contrast to the traditional individual contaminated house paradigm, makes it possible to assess the risk of childhood lead exposure and manage lead hazard in a rational manner. U.S. children are at high risk of excessive lead exposure. Within some groups, the risk is greater than 0.5 for chronic exposures above levels known to be associated with health problems. Inner communities of urban areas have significant accumulations of lead dust compared to small cities. Data from five cities of varying sizes in both Minnesota and Louisiana are presented which support the hypothesis that the major problem is due to lead dust accumulation. Evidence is presented that lead dust accumulation is more closely related to traffic congestion than measures of lead-based paint.

A lead dust cleanup and containment project in inner-city communities of the Twin Cities demonstrated that the proposed paradigm suggested a scientific foundation for risk management. Two groups of children were selected, one in Minneapolis that obtained assistance in lead dust cleanup and containment, and the control group in St. Paul that received no assistance. In the cleanup group of children, 52% showed decreases, 4% showed increases and 44% remained the same compared with the control group children, in which 29% of the children showed decreases, 53% exhibited increases and 18% remained the same. The differences were significant (p-value = 0.0061) between the groups. The largest improvements were at the highest levels of exposure. In the lead dust cleanup group, no children had blood lead above 25 ug/dl, but 24% of the control group did. In the control group, 18% exhibited blood lead of 40 ug/dl or greater at the end of the study period. If they had not been in the study, these poisoned children would not have been identified nor treated. The lead dust contaminated community paradigm provides a basis for making lead risk management an attainable goal among the most lead exposed inner city children.

Hydrochemical Processes In Groundwater Related To Artificial Recharge.

BY

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ABSTRACT

The effects of recharging an esker aquifer with river water is investigated. The thrust has been into the hydrogeochemical part of the problem, with a study of the variation of the major ions temporally as well as spatially. The approach is to find out the available ions in the system, then to define a pre-infiltration composition of the groundwater as a reference and finally to carry out a descriptive statistical and correlation analysis of the major ions. Temporally the data encompasses 30 years (1956-1986) and spatially approximatelly 3.3 km. By also considering the geology, the recharged and the recovered amounts of water, a scenario is presented for explaining the variations of the studied system. Briefly the conclusions are as follows: The infiltration causes an increase of (Cl^- + SO_4^{2-} + NO_3^-) while HCO_3^- decreases, hence abundancy of carbonate species buffers the system. No consistent longterm trend of any ion is detected though for some ions a temporal change has occured. Dilution and oxidation has been found to be the main processes altering the ionic composition of the groundwater.

DISCRIMINATING DIFFERENT SOURCES OF GROUNDWATER CONTAMINATION CAUSED BY INDUSTRIAL WASTES IN THE BESOS RIVER BASIN (BARCELONA, SPAIN)

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Industrial waste accumulation is becoming an important problem in industrialized areas because of the absence of proper management. In Catalonia (Spain) the problem of hazardous wastes is especially serious because of the 500.000 Tn yearly production.

The most frequently found effect is groundwater contamination. Contamination processes are difficult to eliminate and persist for years. Technical solutions are expensive and difficult to apply.

This paper discuses the current situation of the Besós River Basin aquifers affected by uncontrolled dumping of industrial wastes.

The Besós River Basin is located to the north of Barcelona, between the Catalonian Central Basin and the Catalonian Coastal Ranges, occupying an aproximate surface of about 1000 km^2.

Most of the needs of the urban and industrial sites along the rivers draining the Besós basin are supplied by groundwater from the alluvial aquifers of the area. In the La Llagosta basin, the most important aquifer of the zone, the consumption of groundwater represents more than 50 % of the total demand.

Waste associated with chemical, metallurgical, tanning and textile industries, paper mills, food manufacturers, etc. has damaged the quality of the water supply in 3 ways:

1) Old gravel pits filled with urban and industrial wastes.

2) Uncontrolled dumping of industrial wastes

3) Dumping of industrial liquid waste through injection wells or through industrial sewer systems in bad conditions.

Hydrochemical effects of these three types of contamination foci are very similar: leachates or waste liquids easily reach the unprotected saturated zone and cause contamination of domestic and industrial wells. These highly polluted liquids damage the groundwater quality inducing a contamination of organic and inorganic nature, characterized by: high Ec (1500-2000 S/cm), large

proportions of $SO4^{=}$, Cl^{-}, Ca^{2+} and Mg^{2+}, high concentrations of Fe^{2+} and $Mn^{2=}$, presence of heavy metals (Zn, Cr(VI), Ni, Sb, As, Pb, Cd) and phenols, organic micropollutants, etc.

Application of multivariate statistics, mainly Principal Component Analysis, to the raw data of La LLagosta basin brings out the subtle variations between the 3 main sources of contamination, locating and differentiating these foci, even the unknown ones.

About 20 % of the surface of alluvial aquifers (16 Km^2) of the Besós Basin is occupied by old gravel pits filled with wastes.

The impact of industrial liquid waste through injection wells can be seen in the groundwaters of the industrial areas of Granollers, Les Franqueses and Canovelles, where high concentrations of NO_3, Cl and the occasional presence of heavy metals and organic micropollutants are reached.

In other areas of the Besos Basin, such as the Tenes alluvial aquifer, the presence of Cd, Cr, Hg and Cu has been detected, with highest levels found again near old gravel pits.

THE ROLE OF CHLORIDE IN THE SOLUBILITY AND THE TRANSPORT OF URANIUM.IN AQUEOUS SOLUTIONS AT 25°C, 0.1MPA.

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Earlier works have established that, in acidic solution, uranyl (VI) ions react with chloride anions to form mononuclear weak complexes according to the reaction (1):

$$UO_2^{2+} + n\ Cl^- = UO_2Cl_n^{(2-n)} (n=1,2) \quad (1)$$

In neutral solution, only uranyl hydrolyzed species were found to be predominant. Raman spectroscopy has proven to be an useful tool to identify the aqueous uranyl species. The assignment of species is based on the linear relationship between the shift in the O-U-O symmetrical stretching frequency and the number of ligands coordinated to each uranium atom center in the given species. This relationship confirms the presence of the UO_2^{2+}, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^{+}$ but also indicates that a species with the stoichiometry 3:4 (UO2:OH) is present in solutions containing chloride ions. This finding has been interpreted as evidence for a mixed complex: $(UO_2)_3(OH)_4Cl^+$. Its formation reaction can be written as:

$$3\ UO_2^{2+} + 4\ OH^- + Cl^- = (UO_2)_3(OH)_4Cl^+ \quad (2)$$

One additional uranyl(VI) hydroxochloride complex has been identified similarly at more neutral pH. Potentiometric titrations were used to determine their compositions and relative stabilities at ambient conditions.

In basic solution, chloride ligand appears to have no influence in the complex formation with uranium (VI).

Results obtained from the present study indicate that neutral aqueous solutions, with sufficient chloride concentrations, can increase the solubility of uranium(VI). Dissolved uranium can then be transported as $(UO_2)_m(OH)_nCl_p^{(2m-n-p)}$.

ENERGY RESOURCES AND THE ENVIRONMENT: INFLUENCE OF NATURAL BORON EMISSIONS ON SOIL CHEMISTRY OVER TWO GEOTHERMAL RESOURCES IN NEW ZEALAND

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Boron is a major constituent of geothermal fluids. Although concentrated in the liquid phase, over-time significant quantities of boron can be transported as a vapour. In some instances, the condensation of such vapour can yield boron-rich fluids in the upper sections of a geothermal system.

This study was initiated to investigate the level of boron in soils overlying two typical low-enthalpy, (reservoir temperature 120°C) sediment-hosted geothermal resources at Naike and Whitford in the North Island of New Zealand. Boron concentrations in spring and well discharges in these areas are 12 - 16 mg/kg.

In both areas, samples from the A and B soil horizons were taken on a grid pattern at intervals of 250m. Following drying and disaggregation, the boron was leached from the soil, with analysis of the leachate performed using ICP-AES. Acid and hot-water leaching agents were investigated, the latter being most effective.

The highest soil-boron concentrations invariably occur in the A horizon, and a close B-organic matter (LOI) correlation was found to exist. In this horizon, plant-available boron attained concentrations of up to 9.60 mg/kg: two to three times the level which can be tolerated for optimum plant growth.

Soil-boron levels were independant of topography and lithology, being greatest around hot spring areas due to water-B contamination. However, elevated boron level were also found near or over proposed unflow structures, and these are probably the result of the accumulation of vapour-borne boron.

GROUND WATER CONTAMINATION WITH FLUORIDE IN THE CTALAMOCHITA RIVER BASIN, PROVINCE OF CORDOBA, ARGENTINA

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A geochemical study of ground water hosted in loessic sediments of the Ctalamochita river basin, in the Pampa plain region, province of Córdoba, Argentina, has been performed. The area covered approximately 20,000 km^2, located between long. 61°45'W and 6430'W, and lat. 31°40'S and 33°10'S.

Physicochemical parameters, dissolved solids and some trace elements (As, Se, V, Mo, U) were determined in 150 selected groundwater samples. Alcali-metal type waters (sodium is the dominant cation) clearly prevail when cation composition is taken into account; mostly no-dominant type, some bicarbonate- or sulfate-type, and a few chloride-type waters, when anion composition is considered. All samples are alkaline (pH ranges from 7.1 to 8.7), 53% being slightly saline, 29% moderately saline, and 15%, non saline; 55% of the samples are very hard, 31% soft, 13% moderately hard and 11% hard waters.

Systematic and accurate F measurements were performed. Fluoride content ranges from 0.051 to 6.29 mg/l. Over 38% of the samples analyzed exceed the maximum fluoride concentration established by the U.S. National Interim Primary Drinking Water Regulation (1.8 mg/l for an average annual maximum temperature of 17.7-21.4°C). In addition, a strong natural contamination with arsenic and selenium, and high vanadium, molibdenum and uranium contents in ground water has been found.

Sediment samples collected from wells below the C-soil horizon and above the water table were analyzed. The dominant sediment is a clayey silt (average composition in percent: 60 silt, 25 clay and 15 sand). Its mineralogical composition shows dominant feldspars (45-70%); volcanic glass is an important component

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(25-50%; average: 35%) and minor amounts of lithic fragments of volcanic rocks, quartz, muscovite and neoformed calcite and gypsum, as well as scarce opal and chalcedony, were also found. The most abundant heavy minerals (less than 8%) are hypersthene, augite, hornblende, lamprobolite and biotite. Low-crystallinity clay minerals are present, illite prevailing over smectites and interstratified illite-montmorillonite; scarce montmorillonite, kaolinite and interstratified chlorite-montmorillonite have also been identified. The fact that the components of volcanic origin are abundant in this sediment and may be dominant in some sediment samples decides the comparison of the results obtained with the chemical composition of volcanic rocks. Its average composition corresponds to that of a dacite. The composition of the volcanic glass is typically rhyollitic (average SiO_2 content: 72%).

A great variability has been found in the chemical composition of the ground waters from the Ctalamochita river basin. An increase in salinity and hardness values in the sense of the runoff flow is accompanied by many changes in ionic composition: bicarbonate-type waters gradually become no-dominant-, sulfate- or chloride-sulfate-type waters; cation composition changes from calcic-type to calcic-sodium-type and to dominant sodium-type waters. These changes in composition are accompanied by an increase in fluoride contents which reach maximum values in sodium sulfate or sodium chloride-sulfate waters.

The high pH values (7.1-8.7) and remarkable anomalous SiO_2 contents (4.47-192.5 mg/l) in ground water, and pH values in sediments, reveal favourable conditions for the dissolution of the components of volcanic origin, mainly volcanic glass, which may be considered the most important ground water contamination source in the Ctalamochita river basin.

BIOGEOCHEMISTRY OF FOREST ECOSYSTEMS OF THE KOLA PENINSULA

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An ecosystem can be considered to be a complex of relatively autonomous components interacting with biogeochemical cycles. A fruitful way of characterizing the functioning of forest ecosystems is to analyse the biogeochemical interactions between the vegetation, soil and atmosphere.

The biological layer consisting of the biocoenosis (phytocoenosis) and organogenic horizon of the soil plays an important role in the formation of northern forest ecosystems. The capacity for biological cycling of mineral elements in the ecosystem is determined by the number of different elements in the biological layer.

The major part of the biophylic elements in the biological layer is tightly bound and not easily leached.
The poor solubility of these elements is due to their biogenic accumulation in the perennial plant tissues and to their selective incorporation into the humus in the organogenic horizon of the soil. Only a small part of the elements that belong to the biological cycling capacity can participate in exchange processes. The exchangeable pool of these elements is the sum of the following components: 1) leached from the canopy, 2) released during decomposition of plant material, 3) deposited from the atmosphere, 4) leached from the organic horizon of the soil. The exchangeable pool describes those elements that can be potentially involved in the exchange reactions of biological cycling.

In reality only 50-80% of the exchangeable pool is involved in exchange reactions. The rest of the elements form the reserve pool. The reserve pool includes the elements deposited from the atmosphere and released during decomposition of organic plant matter minus the elements bound in production.

The functioning of the forest ecosystems of the Kola Peninsula is defined by the magnitude of the exchangeable pool and the reserve pool.

The ecosystems in a transitional state are characterized by a more prolonged stability due to the fact that the size of the exchangeable and reserve pools is still considerable. In the autonomic terrain where these parameters are relatively insignificant the ecosystems are much more sensitive to external disturbances.

PHOSPHATE COMPLEXATION AT THE SURFACE OF GOETHITE

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Reactions at the solid/water interface of suspended matter greatly influence the speciation and transport of many components in natural water systems. This is e.g. the case for phosphate, for which the bioavailability can be limited by adsorption reactions.

In this work the complexation reactions of phosphate at the surface of goethite (α-FeOOH) has been studied. Goethite is considered as the most common iron oxide in soils and is known to be a strong sorbent of organic and inorganic ligands as well as metal ions.

Equilibrium measurements in the $-\log[H^+]$ range $3 \leq -\log[H^+] \leq 9$ were performed as potentiometric titrations using a glass electrode (0.1 M $Na(NO_3)$ medium, 298.2 K) supplemented with spectrophotometric phosphate measurements. Stock suspensions of goethite (11 $g \cdot l^{-1}$) were prepared by alkaline precipitation.

The complexation of phosphate to the goethite surface was found to be strong within the whole investigated $-\log[H^+]$ range.

The experimental data were evaluated on the basis of the constant capacitance model and with the aid of the computer program FITEQL version 2.0.

The phosphate complexation are described by a model including the following equilibria:

$$\equiv FeOH + H_2PO_4^- \rightleftharpoons \equiv FePO_4^{2-} + H^+ + H_2O$$

$$\equiv FeOH + H_2PO_4^- \rightleftharpoons \equiv FePO_4H^- + H_2O$$

$$\equiv FeOH + H_2PO_4^- + H^+ \rightleftharpoons \equiv FePO_4H_2 + H_2O$$

Further evidence for the proposed model is given by zeta-potential measurements.

THE USE OF MOSSES IN GEOCHEMICAL AND ENVIRONMENTAL STUDIES IN FINNISH LAPLAND - COMPARISON OF RESULTS FROM 1982 AND 1990

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Mosses are known as good monitors of airborne contamination and this sample media has been successfully used in studies of areal distribution of deposition of heavy metals. In addition to airborne metal deposition the local geochemical composition of soil and bedrock may affect the chemical composition of mosses. Mineral particles originating from the trees and dust from surrounding mineral soil can effect the elemental concentrations. However, this effect has not been thoroughly studied.

A regional sampling of mosses has been carried out during the Nordkalott project in 1982-1983 in Eastern Finnish Lapland and repeated in whole Finnish Lapland in 1990. Because mosses collect metals with their living year-shoots the metal content is cumulative value collected during 3-4 years. The repeated sampling with interval of seven years will offer a good basis for the estimation of trends in airborne deposition. The geochemical signature should remain constant. Therefore changes in elemental concentrations can be related to anthropogenic sources. Because Finnish Lapland is affected only by emmissions from a few sources the distinction between anthropogenic and natural variation can be seen.

Clear effects in metal concentrations caused by industry, mining and processing of metals was noticed in different parts of the study area. These metals eg. Ni, Cu and V originate from local emission sources as well as longdistant emission sources in Kola peninsula and the concentrations exceed up to ten times the natural variation of these elements. In addition some elements eg. Y and Cr reveal differencies in geochemical composition of soil. Concentrations of macronutrients (Ca, P, S, Mg) in moss do not clearly reflect the variations of these elements in their surroundings. Probably the high natural concentration of these elements in moss smoothens the variations caused by deposition and natural impact.

TRANSPORT OF THE CHERNOBYL FALLOUT IN SOIL AND BEDROCK - A FIELD STUDY

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After the Chernobyl accident in April 1986 large areas of Sweden were exposed to considerable wet and dry deposition of radionuclides. As part of the SKB (Swedish Nuclear Fuel and Waste Management Co) program for biosphere studies, a small catchment area, Gideå, in northern Sweden was selected for a detailed study. The study was to identify the consequences of the fallout on soil and water chemistry, and to describe transport paths and transformations of nuclides in soil and water. The study can be regarded as a large-scale tracer test, where the tracer enters the soil and groundwater as a non-point temporary source over the entire drainage area. This paper presents study results, and addresses problems when interpreting transport processes using sparse data.

Several different nuclides were detected in a packed-off section, at a depth of 100 m, in a well drilled into granitic bedrock. Ground deposited nuclides were transported to these depths through the bedrock fracture system, with travel times as short as 9 months. Time series from four years of measurements of nuclide activity (Rutenium-106, Cobalt-60, and Cesium-137) in the well were evaluated using simple transport models to determine travel times, estimate the amount of hydrodynamic dispersion, and identify retardation of nuclides. Measurements in soil profiles provided supplemental information of relative amounts of nuclide that may have entered the bedrock fracture system at the surface.

As sampling and analysis of nuclides in this case was costly and time consuming, only a limited number of measurements were available. This situation is not unusual in environmental sciences, as one must often interpret processes on the basis of sparse data. In an attempt to enhance the practical possibilities of interpreting sparse data, several data sets (time series of nuclide activity) were used simultaneously in inverse modelling. The inverse modelling entailed estimation of transport parameters by non-linear regression. When parameter estimation was performed on several chemistry data sets simultaneously, estimation errors of parameters were reduced, and thereby providing a more reliable basis for interpretation of nuclide transport processes.

In addition to contributing to the knowledge of contaminant migration paths in natural water systems, the results give some specific information about transport behavior of the investigated nuclides. The results show that Cobalt and Cesium are retarded compared to Rutenium. Further, Cesium appears to be affected by different chemical processes than the other nuclides, an effect also indicated by speciation analyses of the water samples.

CHEMICAL REACTIONS IN DISCHARGE AREAS AND THEIR IMPORTANCE FOR THE CHEMISTRY OF RUNOFF WATERS

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Recent research in Sweden has shown that most of the runoff in streams has passed through the groundwater zone. In the discharge areas both acid-base and redox-reactions can be important for the chemistry of the runoff waters. Seven micro-discharge areas having a size of about 3-4 m^2 have been investigated. Most of them are upper reaches of streams in coniferous forest usually filled with peat and mosses. Groundwater, soil water and runoff water have been sampled. Peat was sampled and fractions of aluminium, iron and manganese were determined by separate extractions with 1M KCl, 0.5M $CuCl_2$ and 0.2M $(NH_4)_2C_2O_4$. The fractions associated with the different extraction solutions are exchangeable, organically bound and amorphous hydroxide. The total amounts of Al, Fe and Mn were determined as well as for the base cations.

Aluminium, iron and calcium are the major cations in the peat of non-acidic as well as acidic areas. Fe was predominanty present as amorphous hydroxide whith an accumulation in the zone of water table fluctuation. Second important was the residual ranging from 1-40 % of total Fe. The Al chemistry was more complex and seemed to be differ between areas. In some areas the amorphous hydroxide-Al and a residual fraction dominated. In other areas there is an overlap in Al-hydroxide and organically bound Al which together are 150-200 % of total Al. One explanation is that the extraction solutions are not selective and it is also usually assumed that ammoniumoxalate extract amorphous Al-hydroxide as well as organically bound Al. Al-hydroxide surfaces may also be covered with adsorbed organic matter. Aluminium in such positions may be extracted with both $CuCl_2$ and $(NH_4)_2C_2O_4$. It had been shown in other studies that the DOC adsorbtion is at maximum near pH 5.0 , a pH close to the values in the areas with high organically bound Al. The water analyses indicated that the discharge zone is a sink for DOC as the concentration in the water decreased on the passage through the zone and which may be due to microbial and/or chemical immobilization. Al present in several forms may indicate that it orginates from different processes and different soil horizons either organic or mineral horizons respectively.

The large amount of total aluminium in the peat show that the discharge zone is an important zink for the element. The process of aluminium retention and also the DOC-retention in this zone has potentially important implications for the stream ecosystems.

From the water analyses it seemed that a great part of the peat is sulphur reducing but no difference in sulphate concentration was noticed between runoff water and groundwater. Probably much of the water is stagnant and will not contribute to the runoff. The sulphur reducing capacity of the peat can explain some of the large residuals for Fe as it can be precipitated as sulphide.

IMPORTANCE OF HYDROLOGY IN THE REVERSAL OF ACIDIFICATION ON THE TILL SOILS AT GÅRDSJÖN, SWEDEN

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The area around Lake Gårdsjön on the Swedish west coast is one of many where acid deposition has led to surface water acidification. In 1989, a project was begun to study the prospects for reversing surface water acidification by significantly reducing the input of acid deposition. This is being done with a 6,300 m^2 roof which has been built over an acidified catchment to intercept the acid deposition and, starting in April 1991, replacing it with artificial precipitation that has a chemistry closer to that of the pre-industrial period.

To develop the understanding of how water's movement within the soil effects the reversal of acidification, a hydrological research program is being conducted in conjunction with the roof project.

Previous research has indicated that near-surface soil horizons, temporarily saturated when the groundwater table has risen, constitute a dominant flow pathway for storm runoff. The implications of these flow pathways for runoff chemistry, and specifically for the reversal of acidification, are central issues for the research program. The residence time and mobility of water along different flow pathways is considered particularly essential for the quantification of hydrochemical processes, such as weathering, an increase in base saturation, and any eventual desorbtion of sulfate stored in the catchment soils. The well defined boundaries of the catchment will make it possible to account for the storage and flux of water which will be used as a basis for further hydrological analyses.

The three major components of the hydrological research program are detailed hydrometric observations, tracer experiments and the use of physically based models.

^{18}O-content in lakewater, used as precipitation under the roof, is 1-2 per mille higher than that in the pre-treatment runoff water. When sprinkling begins there will be a catchmentwide injection of water with a ^{18}O-content significantly different from water stored in the catchment. By following the changes inside the catchment, and at the outlet, information about residence times for water will be obtained. There have also been injections of radioactive tracers in different soil layers and locations within the catchment. This gives an opportunity to investigate single flow pathways, particle velocities, residence times in various parts

of the catchment, and the spreading of water by dispersion.

Initial results show that hydraulic conductivity (K) is considerably higher in the upper soil horizons than in the deeper ones. An average of some 100 samples from all horizons gives $K=7.0 \cdot 10^{-5}$ m/s. For A- and C-horizons, $K=1.6 \cdot 10^{-4}$ and $4.7 \cdot 10^{-5}$ m/s respectively. The first tracer experiment with ^{3}H och ^{36}Cl shows that high water particle velocities occur in the soil, up to 1.5–3 m/h in the area just upslope the catchment outlet.

MAPPING BASE CATION BUDGETS FOR SWEDISH FOREST SOILS

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Base cation budgets for forest soils are important with respect to soil conservation and crop management. There are reasons to believe that increased biomass production followed by stem och whole tree harvest, temporararly or permanently, might result in negative budgets for selected elements. In fact, resampling of soils at several forest sites in Sweden have shown that the pool of exchangeable base cations have been depleted during the last decades. The depletion is usually explained by increased base cation leaching due to atmospheric deposition of acids and by an increased uptake in forest biomass as a result of improved forest production. Negative budgets can result in temporary deficits for essential nutrients during periods of high forest growth, e.g in young stands during the vegetation period or eventually permanent deficits.

Base cation budgets are calculated using mineral weathering rate and deposition as input and biomass removal and leaching as output. The calculation is carried out for Ca, Mg and K at about 1500 sites on till soils of the National Forest Soil Survey. Weathering rate was estimated according to the model presented by Olsson and Melkerud (1991). The model is based on the geochemical composition of the C horizon and temperature climate. Base cation deposition was estimated by the Swedish Environmental Research Institute using EMEP and national monitoring stations (Gun Lövblad in prep.). Base cation uptake in forest biomass (removal by harvest) was calculated for the 1500 sites using the the HUGIN model (Bengtsson et al. 1989), combined with biomass functions (Marklund 1988) to estimate biomass growth and selected Swedish biomass investigations to estimate nutrient concentrations in different biomass fractions. Base cation leaching was assesed for each site by regionalizing results from about 50 catchment studies distributed all over the country.

The areal distribution of the budgets [weathering + deposition - harvest (stem or whol tree) - leaching] are diplayed on maps for Ca, Mg and K. The area showing negative budgets ranks in the following order: whole tree harvest >> stem harvest and Ca > K > Mg.

THE USE OF GEOCHEMICAL DATA IN APPLIED ENVIRONMENTAL STUDIES

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A national biogeochemical mapping programme is carried out by the Geological Survey of Sweden (SGU). Replacing inorganic stream sediments, plant roots from stream banks and aquatic mosses are sampled. These reflect the contents of heavy metals in stream water. Research has shown that roots and mosses respond closely to chemical background variations related to different bedrock types. They also reflect in a sensitive way the effects of pollution.

Aerial parts of plants do not, in general, respond to high heavy metal concentration in the growth medium. This is due to the fact that plants have physiological barriers between roots and above-ground parts protecting them from uptake of toxic levels of heavy metals into the vital reproductive organs.

In the national programme the sampling density is 16 samples per 100 square kilometers and each sample point represents a drainage area. The geochemical patterns are primarily related to the geochemistry of the bedrock. Superimposed on these patterns are, however, patterns related to human influence such as airborne pollution and agriculture. An important aspect is also the effect of acid rain on the mobilization of heavy metals in our environment. Knowledge of such patterns is essential for the environmental control program.

The anthropogenic patterns must be distinguished from the natural patterns in order to make the geochemical investigations efficient. This is crucial in all types of geochemical investigations. Therefore we use statistical methods in order to distinguish between these patterns.

Studies have also shown that the method can be used in widely different climatic conditions such as desert areas as well as tropical areas.

AGRO-ECOLOGICAL AND BIOCHEMICAL ASPECTS OF USING THE MUNICIPAL AND INDUSTRIAL WASTES AS ORGANIC FERTILIZERS

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A considerable amount of organic fertilizers is requered for the soils of nothern humid areas in order to support their humus balance without deficit. Thus it is necessary to use along with manure and peat such a nontraditional fertilizers as sapropel, deposits of sewage waters, fish flour, ocean algae and other natural organic substances such as sawdust, bark, hydrolyzed lignin and also different municipal and industrial wastes. The solution of the problem of the utilisation municipal and industrial wastes (for example, hydrolyzed lignin) is not of only economic, but also of ecological importance.

Effective methods of composting are worked out for the hydrolyzed lignin and other analogous materials. Composting with poultry manure is among them. Physical-chemical investigations of hydrolyzed lignin and poultry manure-lignin compost were held. Particularities of their structure have been studied by the electron-microscopic method. Wood fragments of hydrolyzed lignin had different degree of decaing depending on the time of composting. 4-50 mcg/g of Zn, Co, Cu, Mn, Ni have been found in hydrolyzed lignin. But calculations showed that the accumulation koefficient of this elements amounted to thousandth and hundredth parts if to use poultry manure-lignin compost every year. Fertilizing soil with optimal doses of this compost leads to increasing yields of grass, grain crops, potato. Humus condition of the soil is also improved: C_{HA}/C_{FA} increased from 0.9 to 1.4. Chemical properties of poultry manure-lignin compost hadn't any considerable differences in the comparison with peat-manure compost (40% C, 2% N, 0,5% P, 0,1% K, pH 7).

Before using both the hydrolyzed lignin and other kinds of nontraditional fertilizers a special control for phytotoxity and correspondance to sanitary-hygienic demands are necessary.

Under modern conditions burning any organic materials of nature genesis cann't be considered expedient, because it leads to noneffective using of organic materials and to the atmospheare pollution. It is necessary to return all organic substances into soil and into their biogeochemical cycle and to consider them not only as fertilizing, but also as reclamation matters if there are not any more effective methods of using them.

APPLICATION OF A MERCURY SCREENING METHOD FOR INVESTIGATING CONTAMINATED SITES

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The investigation of contaminated sites requires a stepwise procedure which is generally demanded not least for economic reasons. Therefore great importance is attached on the development of reasonable screening methods as a first step in detailed soil investigation programs. It is the obvious thing to transfer classical geochemical screening methods to those environmental investigations. This can be realized, for example, by the application of mercury as an indicator to various anthropogene soil contaminations.

Since years soil mercury has been used as a pathfinder element in geochemical ore prospecting. Being a time and cost saving tool this method has already been tested successfully for contaminated site identification and delineation (1). Due to these encouraging results a mercury screening survey was carried out in a fallow area in the city of Hannover in summer 1990. This area was suspected to be heavily contaminated by (non-airborne) Pb and Sb emissions from a nearby battery factory and to require remedial action prior to building development. For geochemical reasons the presence of trace mercury was obvious.

The mercury method was specifically applied to identify contaminated zones within the 45 000 m^2 area with the aim to enable selective sampling for detailed multi-element analysis.

Soil samples were collected from the A- and B-horizons in an almost regular grid of 25 x 25 m. Mercury analyses were carried out by flameless AAS in the ENMOTEC-laboratories. The soil mercury distribution shows several anomalous zones which correspond well to anthropogene contaminations as proved by detailed follow-up investigations:

- soil covered dumps containing battery production residues contaminated by Pb, Sb, Cd, PAH's;
- Pb and Sb contaminated slags from the former Pb melting plant of the battery factory;
- digged ditch sediments contaminated by various metals; since 1940 wastewater from the battery factory has been discharged into the ditch.

Although some small soil mercury anomalies detected in this survey still remain unexplainable the results show a fast and reliable screening method giving sufficient information

for follow-up work. The survey was an important basis to select appropriate sample locations for expensive detailed investigation and thus prevented arbitrary decisions. The mercury method is estimated to be a suitable tool for an economic stepwise procedure in investigating contaminated sites whenever the presence of mercury as main, accompanying or trace element is suggested.

Reference:

(1) Appel, D. & Pöppelbaum, M. (1988): Mercury - new ways for an old pathfinder.- Contaminated Soil '88, 2nd International TNO/BMFT Conference on Contaminated Soil, 11-15 April 1988, Hamburg, S. 235 - 237.

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Anthropogenic effects on the mass balance of weathering and erosion

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During geological history of the Earth's surface, weathering of rocks, formation of regolith (i.e. weathered zone including soil) and erosion have proceeded with different rates, depending on tectonic and climatic cycles. From the human point of view, these long-term changes seem to be less important that the short-term changes within the span of several years to thousands of years. Considering this geologically short time, we may assume that weathering and erosion reached a steady state before industrial man. This steady state maintained constant properties and constant quantity of regolith . Because the rate of weathering and rate of erosion depend on the water-rock interaction, even quality of water reached a steady state. Since the well-being of human society depends on supply of clean water and fertile soil, it is very important to protect this steady state of the Earth's surface. Unfortunately, many human activities disrupt this steady state on large territories. Two of the very negative activities from this point of view seem to be the environmental acidification due to emissions of SO_2 and NO_x and intensive agriculture which uses large quantities of industrial fertilisers.

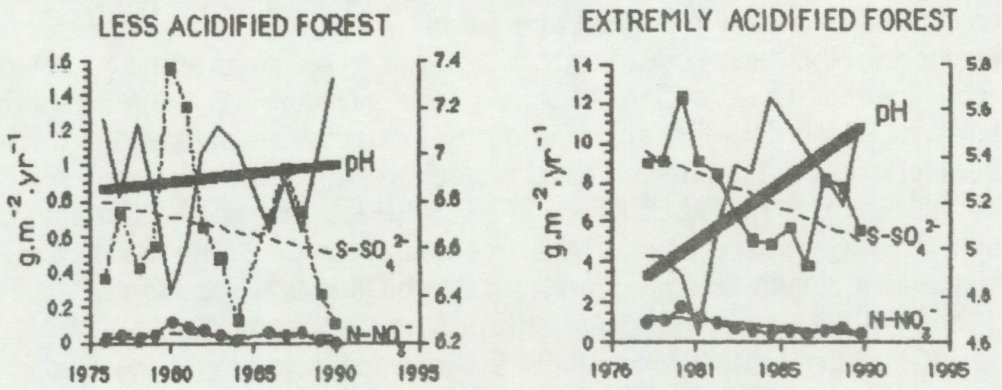
Czech Geological Survey has studied the changes in the rates of weathering and erosion by monitoring biogeochemical cycles of elements in small representative catchments since 1975. The catchments represent forest and agricultural fields in the region with the annual average concentration of SO_2 equal to 8.3 $\mu g.m^{-3}$ and NO_x equal to 11.2 $\mu g.m^{-3}$ and forest with dieback of spruce (Picea abies) where the annual concentration of SO_2 is 112 $\mu g.m^{-3}$ and NO_x is 33 $\mu g.m^{-3}$. By monitoring the amount and chemical composition of atmospheric deposition, runoff, applied fertilisers, harvesting of crop and lumbering of trees a mass balance of Na, K, Ca, Mg, Cl, N, S, Al and Si was evaluated and from that the weathering rate and erosion rate of bedrock (gneiss and granite) and regolith (with acid brown soil) was calculated using a steady state model of Paces (1982, 1985, 1986). This evaluation of field data has proved that the environmental acidification and modern agriculture are changing the biogeochemical steady state between weathering and erosion. The major results are summarised in the following table. The acidification increases the rate of chemical erosion while agriculture increases mostly mechanical erosion. In the monitored catchments, the rate of weathering increases by a factor of 2.3 due to agriculture and by 2.1 due to extreme acidification. The mechanical erosion has increased 2.7 times due to agricultural practicies while the acidification by industrial emissions has increased the mechanical erosion 1.9 times. The chemical erosion has increased only little by a factor of 1.5 due to agriculture while it has increased significantly, 2.9 times, by acidification. The chemical erosion in the forested catchment with dieback of spruce depletes Calcium and Magnesium from the sorption complex of soils replacing them with Hydrogen and Aluminium ions. Presently, the chemical equivalent ratio of $Ca^{2+}+Mg^{2+} / H^{+}+Al^{3+}$ in the sorption complex of the acidified soil

is less than 0.1 while in the less acidified forest it is more than 0.5. This ratio is an important indicator of the disturbed mass balance between chemical weathering and chemical erosion. If the low ratio is harmful to spruce as many physiological studies suggest, than our results indicate that the value of 0.5 may be the critical one. The forests in our catchments with this value show the first signs of damage.

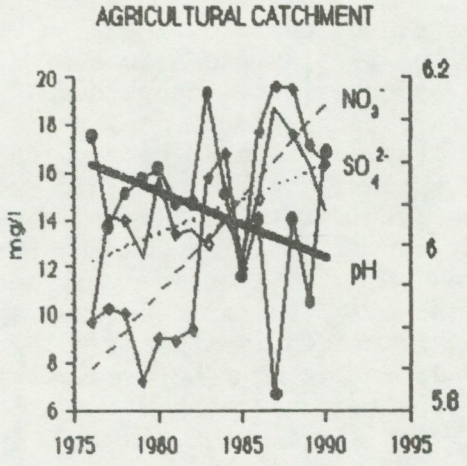
Table 1. Rates of weathering and erosion (in kg $ha^{-1}yr^{-1}$) if not given otherwise.

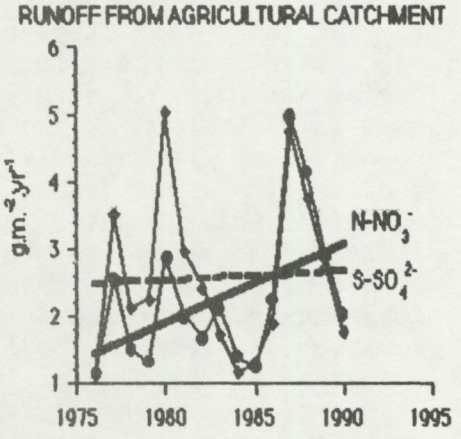
Characteristics of catchment	Forest not strongly acidified	Fields fertilised	Forest dieback due to acidification
Weathering of gneiss	732	1 700	1 510
Mechanical erosion of regolith	732	1 991	1 402
Chemical erosion of gneiss	109	160	318
Consumption of acidity by chemical weathering and leaching of soil in kmol $[H^+].ha^{-1}.yr^{-1}$	1.5	4.1	6.1
Leaching of Ca^{2+} and Mg^{2+} from soils in $keq.ha^{-1}.yr^{-1}$	0.75	0.85	4.3

The 15-year monitoring of the catchments indicates that the reduction of emissions of SO_2 in western Europe reduces acidification even in eastern Europe. This is shown by the trends in the flux of SO_4^{2-} and NO_3^- and in pH of the runoff water from the less acidified and extremely acidified forested catchments:



This is not the case in the agricultural catchments, where pH is still decreasing while the concentrations of SO_4^{2-} and NO_3^- are increasing. The increase is less pronounced when the runoff of the strong acid anions is calculated as indicated by the following figures:





The results from the five catchments in Czechoslovakia indicate that the complex biogeochemical interaction between bedrock, water, soil and biota is influenced by industrial as well as agricultural acidification. Whether these changes are of global importance or not can be answered after more catchments in various anthropogenic climates are monitored and evaluated.

BOREHOLE GEOPHYSICS APPLIED TO THE CHARACTERIZATION OF FLOW IN FRACTURED CRYSTALLINE ROCKS AT MIRROR LAKE, NEW HAMPSHIRE

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The U.S. Geological Survey has designated the Mirror Lake, New Hampshire watershed as the location for an intensive study of flow in fractured rocks where equipment and experimental methods can be developed for use in contamination studies. Although no contamination exists at the watershed, ongoing studies and facilities at the Hubbard Brook Experimental Forest provide an ideal setting for investigations of flow and chemical transport in fractured rock. Conventional geophysical logging measurements such as caliper, temperature, gamma, neutron, gamma-gamma, acoustic, and electric logs provide averaged geophysical properties of rock and fluid in a volume approximately 0.3 to 1.0 meters in diameter. These measurements are generally more sensitive to mechanical enlargement of fracture mouths during drilling and the presence of altered rock adjacent to fracture faces than to the relatively small volumes of permeable fracture openings. However, these volume-averaged measurements are useful in characterizing fractures identified using the acoustic televiewer. Local hydraulic conductivity of fractures within a few meters of the borehole wall can be estimated using the attenuation of waveforms recorded by digitizing the pressure signal produced by a specially designed acoustic logging probe. The local hydraulic conductivities of individual fractures are compared to larger-scale estimates of fracture conductivity determined by packer isolation and pressure testing, and to patterns of borehole flow measured using a recently developed, high-resolution flowmeter during cross-borehole pumping tests. Such comparisons provide important information about how the populations of discrete fractures sampled by individual boreholes are integrated into flow paths controlling contaminant migration in fractured rock masses.

Investigations of fracture permeability at Mirror Lake began by constructing a 10-meter-wide array of boreholes as much as 200 meters deep. This small scale investigation was expanded by additional drilling to produce a line of boreholes about 100 meters apart and extending across the 2-kilometer-wide watershed. Televiewer, acoustic attenuation, and other logs indicate an irregular distribution of locally permeable fractures with depth. Cross-borehole flow measurements indicate that only a small fraction of apparently permeable fractures encountered by boreholes produce or accept flow. The pattern of relative permeability identified from these flow measurements is generally confirmed by the more time-consuming but more quantitative procedure of packer isolation and pressure testing of individual fracture sets. These results indicate that fracture flow paths in the Mirror Lake watershed are formed by the intersections of numerous discontinuous fractures, many with orientations very different from that of the large-scale flow. Comparison of fracture distributions and lithology inferred from geophysical and lithology logs indicates that at least some of the large-scale flow paths are controlled by lithologic contacts.

Sources and mobility of copper and cobalt in a small upland catchment, English Lake District

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Patterdale in the English Lake District contains a small upland catchment, Brotherswater, formed on Ordovician Borrowdale Volcanic Series bedrock, with a well-defined watershed. Deficiencies in copper, cobalt and selenium have been reported in cattle which are farmed in the area.

Bedrock in the Brotherswater catchment consists predominantly of andesitic tuffs (bedded, welded, lithic and unbedded fine-grained), with occasional andesitic/rhyolitic lava flows. The superficial deposits include morainic and outwash material of probable local origin: soil development is poor and has progressed through and since the Late-Devensian. Two of the elements causing deficiency problems, copper and cobalt, have been determined in representative samples of weathered and unweathered bedrock, in overburden, and in water and sediment samples from stream channels and Brotherswater Lake. Levels of copper and cobalt in the parent material are not significantly low, but the association with mobile particulate phases is high, so the retention time within the grazing environment is very low.

The concentrations and nature of mobile particulate matter have been determined. Concentrations of suspended sediment at falling and low flow conditions from the main lake inflow generally range between 0.1 and 1.0 mg l^{-1}, compared to a maximum rising-flood concentration of 200 mg l^{-1}. Mineralogical and particle-size investigations carried out on suspended particulates indicated a particle diameter less than 64 μm excluding flood samples, and an assemblage of quartz, plagioclase feldspar, chlorite and illite - the same minerals which were present in the bedrock, soil and lake sediment. The organic content and Fe oxide component of mobile particulates are relatively high, and partially control the association of Cu and Co.

We conclude that it is important to integrate data on sources and levels of essential trace elements and their particulate associations with hydrologic information in order to predict element mobility and related deficiency diseases in upland catchments.

SOME CHEMICAL CHARACTERISTICS OF SEDIMENTARY SOILS IN THE MEDITERRANEAN ENVIRONMENT: A COMPARISON OF UNDISTURBED AND DISTURBED SOILS

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Of the numerous relations which unite the different components of an ecosystem, the distribution and circulation of minerals is one of the most important. The interest in mineral cycles has grown in recent years, during which several detailed studies of ecosystems in temperate zones have been published.

The equilibrium of these cycles is very fragile, and there exist numerous factors -abiotic, biotic and, above all, human- that constantly disturb it. Human interference in natural ecosystems generally alters the availability of nutrients, reducing the productive potential of the soil and creating, in same cases, very destructive perturbations. For this reason, an understanding of the proportions of soluble anions that are transported by water in different natural and disturbed ecosystems is key to the initation of studies of mineral cycles.

In many ecosystems, especially in silicious soils, the balance of mobile anions controls the entire ionic equilibrium of the ecosystem. These anions primarily come from the atmosphere or as a result of the activities of living organisms, and to a much lesser degree from rocks and soils. Sulfate, for example, comes from precipitation and is the predominant anion in soils in northern Europe. Nitrate is also in part of atmospheric origin; it is the most important anion in agricultural ecosystems. Finally, chlorine is of atmospheric origin as well.

Of the anions which we are going to study, some are key elements for plant growth (nitrates, phosphates and sulfates), others are important for the nutrition of soil organisms and still others are elements generally found in trace amounts and which can be deletereous or toxic for animals and plants (for example, fluorine). Information about soluble anions in different soils is rare, because most studies have focused on the soil-plant interaction, given that it is generally very difficult to detect the often low levels of these minerals found in the soil.

In our project, we are studying the principal anions found in the superficial layer of soils situated over sedimentary substrates in the continental mediterranean environment, primarily in semiarid regions. These soils have been altered to a greater or lesser degree by human and animal activity. They are degraded and eroded, and in some cases have been strongly disturbed as a result of being used as disposal sites for solid waste from urban areas. These altered soils will be compared to samples taken from less disturbed areas in order to highlight the changes.

GEOCHEMICAL MAPPING: A COMPARISON OF THE USE OF ACTIVE STREAM SEDIMENTS AND SOILS, WITH SPECIAL REFERENCE TO WALES, UK.

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Extensive geochemical sampling surveys leading to the production of large scale distribution maps have been performed throughout the world in recent years. Mapping has been carried out using various different substrates as sampling media; active stream sediments, soils, waters and plant species are all commonly used. However, little attempt has previously been made to compare and evaluated the use of different substrates for the construction and interpretation of geochemical maps.

In order to facilitate such a comparison, the maps presented in The Wolfson Geochemical Atlas of England and Wales (Webb *et al.*, 1978) were compared with those produced for Wales by Paveley (1988). Webb and his co-workers sampled active stream sediments at a density of $1/2.5Km^2$; whereas Paveley analysed composite soil samples (both upper (0-15cm) and lower (15-50cm) horizons) taken from profiles throughout Wales (an area of 20,250 Km^2), on a regular 5Km grid. Maps produced for the metals lead, zinc, copper, cadmium, cobalt, nickel and manganese have been examined and evaluated.

Many anomalies of elevated metal levels were observed in both surveys. In general, there was a good agreement between the two sets of data. For example, the distribution of the metals lead, zinc, copper and cadmium normally associated with sulphide mineralisation show similar patterns in both sets of maps. This essentially reflects the distribution of contamination from previous metal mining and processing activities. Similarly, the manganese ore beds of north west Wales are highlighted by both sets of data.

However, some interesting differences between the two surveys have also been noted. For example, cobalt and nickel anomalies observed in soils in North Wales are not revealed to the same extent by stream sediments. This is surprising as these high concentrations would seem to be related to the shale bedrock of the area, which one would expect to be reflected in the composition of stream sediments. Patterns of elevated soil lead, zinc, copper and cadmium levels revealed around Milford Haven and in the Vale of Glamorgan are also not evident in the stream sediment maps. The Milford Haven anomaly, in an area where there are extensive oil refineries, was thought to be a result of atmospheric deposition of pollutant heavy metals and concealed mineralisation is likely to be responsible for the high soil metal values in the Vale of Glamorgan.

General conclusions concerning the appropriate use of soils and active stream sediments as sampling media for the production of geochemical distribution maps have been made, with reference to element sources, collection of substrates, sampling density and the nature of the environment.

Paveley, C.F. (1988) Heavy metal sources and distribution in soils, with special reference to Wales. Unpublished PhD thesis, University of Bradford.

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Maciej Pawlikowski/x

Investigation of human tissues mineralization /calcification/ in the aspect of life preservation

Contemporary scientific investigations are focused on the relation between environmental conditions and a human organism, but biological processes especially processes of human tissues mineralization develope independently on polution of environment.

The mineralization of human tissues leads to their destruction and tisturbances of biological activity. The effects of these disturbances are known as ilnesses and very often are the reason of the death of the organism.

Crystals growing in the human body differ crystalographically as well as chemically. They are observed in the brain, . blood vessels, pulmonary system , gallblader, kidneys, thyroids, cartilage, bones, teeth, malignant tumors etc.

All these tissues as well as the minerals have been investigated using mineralogical and histological methods.

Obtained results constitute the basis for experiments on crystalization and dissolution of minerals in vitro and in vivo. The effects of all these investigations can be utilized in research on proper functioning of human tissues and therefor can extend the life of the organism.

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METAL SPECIATION IN A POLLUTED HUMIC SURFACE WATER SYSTEM

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Sampling and speciation of trace metals (Cu, Zn, Cd, Fe and Al) were performed in a humic rich surface water system contaminated by leachates from a tailings deposit in a mining area (Bersbo, Sweden). Samples were taken in a stream 0.2 km downstream the deposit (pH 5-6) on four occasions and twice in a lake another 5 km from the deposit (pH 8) during one year.

The samples were filtered through a 1.2 μm-filter in N_2-atmosphere immediately after collection. The humic substances were adsorbed onto a weak anion exchange resin (diethyl-aminoethyl-Sephadex A-25) and the cationic fraction was adsorbed onto a cation exchange resin (sulphopropyl-Sephadex C-25). The metals were desorbed from the resins with 4 M nitric acid and determined by AAS (Cu, Cd, Zn) and ICP (Fe, Al). The humic substances were desorbed with 0.1 M NaOH and determined spectrophotometrically at 250 nm.

The distribution of Fe, Al, Cu and Cd (anionic, cationic and particulate) varied between the two sampling occasions. The increase in pH affected the distribution of metals between the different forms, while the influence of the seasonal variations was negligible. At pH 5 more than 80% of Cu was in the cationic form, but as pH increased the fraction of Cu bound to humic substances increased and amounted to 80% at pH 8. The particulate form contained 50% of Fe at pH 5, but at pH 8 this fraction held the main part of Fe. After being almost completely in cationic form at pH <7, a large fraction of Cd was found in the particulate form, probably bound to Fe. More than 95% of Zn was in the cationic form independently of pH.

For Zn and Cd as well as for low concentrations of Fe, Al and Cu there were no correlation between the concentration of humic substances and the amount of humic bound metal. At higher concentrations of Fe, Al and Cu an increasing fraction of the metal was bound to the humic substances with increasing concentration of humics.

The importance of the observed speciation for the transport properties and redistribution of the elements (Cu, Zn, Cd, Fe and Al) in surface water systems (adsorption to particulate phases, formation of organic forms, sedimentation etc) is further discussed in the paper.

ON THE PODZOLIZATION IN THE GLACIOFLUVIAL MATERIAL IN NORTHERN FINLAND

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This study was initiated to decipher the development of the podzol profile into the sorted glaciofluvial material as a function of its age. The study sites were selected from the west-east line across the northern Ostrobothnia and Kainuu in northern Finland. Altogether 7 study sites situated on the eskers and interlobate complex were sampled. The absolute heights of the sites vary from 2.5 m a.s.l. in the western part to 235 m a.s.l. in the eastern part of the line. The ages of the podzol profiles vary from 330 yr B.P. to over 9000 yr B.P.
The thickness and colour of the different soil horizons, the grain size, water content, and organic matter of the material were determined as physical properties. The specific conductance, pH, redox potential and acid neutralization capacity (ANC) were measured as chemical properties. Also the contents of the readily extractable Al,Fe,Ca,Mg, K,Mn,Zn and Cu were determined by AAS. The total contents of Al,Fe,Ca,Mg,K,Mn,Si,Ti,Cr,P and Ba were analyzed by XRF.
The eluviation horizon (A_2) becomes thinner when the age of the soil increases. The development of the complete podzol profile has taken time of over 300 but less than 1230 years.
The acid neutralization capacity of the illuviation horizon (B) increases with the increasing age of the soil. So the older soil can better resist the acidification. The amount of the base cations necessary for plants is quite small in the podzols developed into the coarse-grained glaciofluvial material.

GEOCHEMICAL CONSEQUENCES OF THE GREENHOUSE EFFECT

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In comparison with the climatological consequences and side-effects (such as a rise in the global mean atmospheric temperature, an increase in cloudiness and windiness in the atmosphere and a general rise in the sea level) the geochemical repercussions of the greenhouse effect have been touched upon only on a very limited scale in the geological and geochemical literature to date. Notwithstanding the little interest, the geochemical consequences of the effect (discussed and reviewed in the paper in more detail) can be fairly dramatic however, involving an enhanced rate of weathering of carbonate rocks, which together with the similar effects of acid rain, will cause deterioration in marble buildings and monuments and may even jeopardize the very existence of oceanic coral reefs by dissolving the limestones in their framework and root zones. Similarly, intensified weathering of silicate rocks will lead to an increase in the dissolved components in natural waters, which may in turn result in public health hazards. The above and other similar ramifications and side-effects (too numerous to be enumerated here) are a result of the conservative policy adopted by Nature in her self-protection against changes imposed by man upon her chemical systems and upon the environment in general. This policy is known in the physical and chemical sciences as the principle of Le Chatelier, which ordains that any change imposed on a natural chemical system in which an equilibrium has previously been achieved (e.g. the addition of a reactant or reaction product) will give rise to a reaction by which the system aims at nullifying the addition and restoring the chemical equilibrium. An increase in carbon dioxide in the atmosphere, the prime cause of the greenhouse effect, will accordingly and along the lines of Le Chatelier's principle engender counteracting reactions such as

(1) $CO_2(g) = CO_2(aq)$

and

(2) $CO_2(aq) + H_2O = H_2CO_3$

which, due to the addition, proceed from left to right thus helping the natural waters to (partially) absorb the excess carbon dioxide. This will mean an increased concentration of carbonic acid in natural waters, however, which in turn, again on the lines of Le Chatelier's principle and the law of mass action, will lead to reactions such as the dissolving of limestone

(3) $H_2CO_3 + CaCO_3 = Ca^{2+} + 2HCO_3^-$

and the hydrolysis of silicate rocks (often accentuated by carbonic acid)

(4) $3H_2CO_3 + H_2O + M_4SiO_4 = H_4SiO_4 + 3HCO_3^- + 4M^+ + OH^-$

with an ensuing reduction in the concentration of carbon dioxide in the air.

ENVIRONMENTAL GEOCHEMISTRY, GEOLOGICAL PROCESSES AND THE GEOCHEMICAL CYCLE

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The geochemical cycle (GC), being a central concept in geochemistry, is therefore of the upmost importance in environmental geochemistry (EG).

The cycle shows the most important migration paths of the chemical elements among the major reservoirs of our planet and refers to the most important geological processes associated to such paths. The primary importance of geology in EG is then revealed by the cycle.

Several diagramatic representations of the cycle are available from different authors, all of them stressing the role of such processes, deep-seated or superficial.

William Fyfe has pointed out that some of the deep-seated processes may have a strong influence on the outmost geospheres and may be potential mechanisms for solving environmental problems.

Let us recall a couple of simple facts:

- Rock genesis and transformation at depth, together with uplift and erosion, are primary causes of differences in element availability on the surface of the crust.
- Deep-seated faults in the crust (continental and oceanic) are pathways for upward element migration.

(These are just two reasons why geologic infomation, including geological maps, is mandatory for the environmental geochemist.)

- Earthquakes and volcanic eruptions are processes surely to be predicted in the future on a sound geochemical basis and this clearly is of the realm of EG.

Environmental geochemistry is mostly concerned with the superficial environment and this made obvious a need for an independent representation of the exogenic cycle. Curiously enough, in such models, from several authors, information relating migration paths to geologic processes is in general missing. So it may be hard for the environmentalist to find out what processes relate to what pathways.

The following are examples, to cite just a few, of processes that should be represented:

- Aerial and oceanic circulation of volatiles and particulate matter of volcanic and continental origin.
- Radioactivity from elements in rock-forming minerals.
- Sea water intrusion.

From the point of view of EG, the GC should be of the biocentrist type, which brings about the role of living matter, and of Man in particular, in the cycling of the elements. It has been argued that the inclusion of the biosphere in the GC diagram makes it too complicated, but the fact is that it is an essencial component of the cycle.

For instance, it is well known that human perturbation of the GC due to excessive use of mineral resources is a matter of great concern. Also biota can suffer the adverse effects of geological processes that deal with element cycling. All this has to do with public -, animal - and plant heath.

A comprehensive diagram of the geochemical cycle is tentatively presented.

BEFOREHAND ESTIMATE OF MASSTRANSFER IN ARSENOFERROUS GOLD MINE TAILING BY MEANS OF MINIPILOT PLANT PROCESS WATER ANALYSIS AND GEOCHEMICAL SIMULATIONS

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Abstract

The tailing minerals have been isolated from an arsenoferrous gold ore by gravity separation method. Tapwater has been used in this process. In order to get a forehand estimate of masstransfer in true mine tailing environment, analyses of process water were interpreted with a USGS mass balance code: BALANCE for mass transfer calculations and a PHREEQE-code for the equilibrium state calculations, and with a LLNL code; EQ3/6 for reaction path calculations.

Mass transfer of the main dissolving/precipitating phases was calculated at five steps (tapwater, separation water, 4 weeks, 8 weeks, 12 weeks) of the process water. Long term equilibrium of water in contact with tailing minerals was calculated with the reaction path code by setting the oxygen fugasity high enough to dissolve all the pyrite in contact with solution.

According to the results, the process water stays highly undersaturated with respect to pyrite and arsenopyrite at every step of the process water but the saturation state is increasing with time. Consequently, hydroxides become supersaturated with time. The mass balance calculations show that pyrite, arsenopyrite, Mn-hydroxide, and Al-hydroxide has left the solution. About 2 mmol/l of pyrite and 0.05 mmol/l of arsenopyrite have dissolved, and 2 mmol of goethite has precipitated in two months. This means that arsenic contents of the process water has increased by 3 mg/l in three months at ambient conditions.

The rate of release will remain constant as far as the process water contains dissolved oxygen, and the dissolved species are transported from the system. In the real world, deep in mine tailing deposite, water is depleted in oxygen and is obviously supersaturated with respect to all the main minerals in contact with water. In this type of semi-closed system, solute transport is slow and concentrations are dependent on the water conductivity, hydraulic gradient, the average flux (darcy velocity), and the concentrations on the surface layer of the deposite.

The final concentrations and equilibration time of water can be calculated with a reaction path code and mass action kinetic simulation respectively. Far-field mass transport that is also essential in environmental risk assesments, can be calculated by means of a coupled equilibrium-mass transport simulation.

NITRATE REDUCTION IN AN UNCONFINED SANDY AQUIFER: PROCESSES AND GEOCHEMICAL MODELLING

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Nitrate distribution and reduction processes were investigated in an unconfined sandy aquifer of Quaternary age. Groundwater chemistry was studied in a series of eight multilevel samplers along a flow line, deriving water from both arable and forested land. Results show that plumes of nitrate contaminated groundwater emanate from the agricultural areas and spread through the aquifer. The aquifer can be subdivided into an upper 10-15 m thick oxic zone that contains O_2 and NO_3^-, and a lower anoxic zone characterized by Fe^{2+}-rich waters. The redox boundary is very sharp, which suggests that reduction processes of O_2 and NO_3^- occur at rates that are fast compared to the rate of downward water transport. Nitrate contaminated groundwater contains total contents of dissolved ions that are two to four times higher than in groundwater derived from the forested area. The persistence of the high content of total dissolved ions in the NO_3^--free anoxic zone indicates the downward migration of contaminants and that active nitrate reduction is taking place. Nitrate is apparently reduced to N_2 because both nitrite and ammonia are absent or found at very low concentrations. Possible electron donors in the reduced zone of the aquifer are organic matter, present as reworked brown coal fragments from the underlying Miocene and small amounts of pyrite at an average concentration of 3.6 mmol/kg. Electron balances across the redoxcline, based on concentrations of O_2 , NO_3^-, SO_4^{2-} and TIC, indicate that pyrite is by far the dominant electron donor even though organic matter is much more abundant. Groundwater transport and chemical reactions were modelled using the code PHREEQM, which combines a chemical equilibrium model with a 1-D mixing cell transport model. Only the vertical component of the water transport was modelled since, in contrast to rates along flowlines, the vertical rates are close to constant as required by the one-dimensional model. Average vertical transport rates of water in the saturated zone were obtained by tritium dating. The modeling process is a two step procedure. First the sediment column is initialized with natural water containing only oxygen as electron acceptor and subsequently agricultural waters containing both oxygen and nitrate are fed into the column. The nitrate concentration of agricultural waters entering the saturated zone varies with time and an input function was therefore constructed by linear mixing of natural waters and agricultural waters. This input function was fed into the column initialized with natural water, and the model run forward in time to the year 1988 where field data are available. Comparison with field data shows that the variation in groundwater chemistry is well described by the model when reduction of oxygen and nitrate by pyrite oxidation are the only redox reactions occurring. Finally predictions are made for the distribution of water chemistry in the year 2003. Downward progression of the redoxcline is accelerated by a factor of five due to nitrate pollution of the aquifer, but absolute rates remain small, on the order of a few cm/yr. The controlling factor for nitrate migration through the aquifer, once it has reached the anoxic zone, is the concentration and distribution of pyrite in the sediments.

ANTHROPOGENIC LEAD CONTAMINATION OF SOILS
-LEAD MOBILITY AND ISOTOPIC RECOGNITION-

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Lead contamination of top soils is mostly caused by gasoline additives. Thus it is anthropogenic. Differentiation of geogenic and anthropogenic lead is easy if the isotopic composition of both sources is sufficiently distinguishable. In past years much of methyl- or ethyl- lead was produced using old ore deposits mostly from Australia. In 1972 two hundred and eighty thousand metric tons of metallic lead were converted into "gasoline lead" in the United States alone. Although much of this lead is distributed over the surface of the earth, part of it is contained in the rust of automobile exhaust. Here it represents the lead source of different age or the prevailing mixtures.
Lead contamination of soils depends on the distance from roads and the density of traffic.
In gasoline samples and car exhaust rusts analysed a range of 206/204 Pb was found to cover 16.305 to 19.165 while geogenic lead in SW Germany has values from 18.4 to 19.6.
Two gasoline additives and eleven car exhausts were analysed for their lead isotope patterns by solid source mass spectrometry. Sixteen soil profiles up to depth of 230 cm below surface were taken and divided into sections. The dried, sieved and agate ground samples were analysed by energy dispersive X-ray fluorescence for five major elements and eleven trace constituents. Homogeneity of soil profiles was found in most cases but along with lead contamination always a bromine increase was observed which definitely originates from the lead additives. Lead increases in top soils locally to more than the tenfold content underneath. If soils developed on sediment material the different compositions of the various supplying areas can be recognised in the horizons by their major and trace element pattern.
Favourable conditions (isotopic patterns) provided mobility of anthropogenic lead can be calculated from depth distribution in soil profiles.

THE INFLUENCE OF NATURAL AND MAN-MADE PROCESSES ON THE GEOCHEMICAL COMPOSITION OF LAKE SEDIMENTS IN NE ESTONIA.

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Using different geochemical and paleontological methods the bottom sediments of some lakes in NE Estonia were investigated. In the reference area there are 39 lakes with different shapes, hydrological regimes and degrees of trophicity, in which deposits with a thickness of up to 7-8 m started to accumulate in the beginning of Holocene in the glaciokarstic hollows. During this century the human impact to the lake ecosystems was remarkable, especially since the 1950s, when the natural water bodies started to incorporate to the systems for technogenic water supply from oil-shale minings. The hydrological regimes of some lakes were changed and atmospheric load was increased by the influence of several thermal power plants. Using the methods of chronology (carbon-14, lead-210, palynology) as well as C/N ratio and loss-on-ignition data, changes of water levels were reconstructed. A complex of geochemical and paleontological data (diatoms) was unable to resolve the causal relations between climatic and hydrologic influence on the geochemistry of the sediments.

In most cases in the upper part (10-20 cm) of deposits the concentration of microelements increased rapidly, becoming up to 2000 times higher than those in deposits formed in similar environmental conditions (about 3500 yr ago).

Special importance were paid to the investigations of postsedimentational processes. The distribution of lead-210 and microelements, and the comparision with the history of human impact shows, that in the lakes studied, where anoxic conditions prevail almost all the year round, the postsedimentational mixing of sediments is rather minor and therefore the distribution of chemical elements, of small migrational potential, mainly describes the primary input. In many cases the discrepancy between the lead-210 time scale and distribution curves of microelements may be detected and possible reasons of this pattern are discussed.

HEAVY METAL CONTAMINATION OF STREAM SEDIMENTS AND SOILS IN THE MINING DISTRICT OF FREIBERG; SAXONY (GERMANY)

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Freiberg is a mining district at the northeastern margin of the Erzgebirge Mts. Since 1169 in this region were mined polymetallic sulphide ores, whose main constituents are galenite, sphalerite, arsenopyrite, pyrite and silver-containing fahlore. In smelting plants up to now were processed not only local ores, but also tin ores from other deposits of the Erzgebirge region.

The environmental medias in the whole region show a strong pollution with heavy metals, especially Pb, As, Cd, Sn and Zn. The main river of this area, Freiberger Mulde, reflects this contamination and its multicausal influences (primary mineralization, mining, metallurgy) by extremely high contents of relevant elements in stream sediments (Table 1).

Table 1: Contents of some heavy metals in stream sediments of Freiberger Mulde river (mg/kg; fraction - 0.2 mm)

	1	2	3
Pb	51	260	660
Zn	223	510	1630
As	25	80	1030
Hg	0,26	0,39	3,6
Cu	33	930	5360
Mo	1	1	5
Sn	10	20	125

1 - background in the non-mineralized erea

2 - after entrance in the ore vein district

3 - after passing the centre of smelting plants

Strong accumulations of heavy metals were also found in soils of flood plains and in the vicinity of outcropping ore veins with tailings of old minings. The vertical distribution of elements varies in dependence of the dominant factor of contamination (geogenic, anthropogenic). The establishment of typ of contamination and distribution of elements is important for chances and technology of sanitation.

THE SCAVENGING EFFECTS OF SAND COATED BY IRON HYDROXIDE IN PHREATIC AQUIFERS

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Sand coated with iron hydroxide was compared with uncoated sand as an adsorbent filtration media for the treatment of metal bearing wastes. In laboratory experiments, the superior performance of the oxide coated sand in the absorption of metals has been demonstrated. (Edwards, M. & Benjamin, M. M. 1989). These experiments were tested in natural conditions. Coated sand as well as uncoated sand was placed in dialysis cells of a multilayer sampler (MLS), (Ronen et al. 1986). The system was used to sample 3 research wells, all located in different environments:

a) a sandy, oxic aquifer, in an area which was irrigated with secondary sewage effluents,
b) a clastic, highly saline (34 % salinity), anoxic aquifer located at the western Dead Sea shore,
c) a chalk aquifer heaviliy polluted by the surface disposal of hazardous wastes.

After several weeks of exposure time in the fields the samples were retrieved and analyzed for the following metals: Sr, Al, Cr, Mn, Co, Ni, Cu, Cd, Pb, Zn. Both pore waters and the quartz grains were investigated using the following methods:

a) extraction by digestion with HNO_3 and analysis by Flame Atomic Absorption Spectrometry,
b) Scanning Electron Microscope (SEM) as well as transmittent light microscope investigations,
c) Microprobe analysis.

Preliminary results have let us to believe that a coated grain causes an increased adsorption of metal concentrations from groundwater. The results from the SEM proof that the iron hydroxide coating prevails in the natural environment and does not disappear. Al, Co, Mn, and in one case Sr show enriched concentrations as compared to the uncoated material. There were no coatings or crusty products detected on the treated material after interaction with the groundwater.

It is our belief that the Fe-Hydroxide coating can play a role as scavengers for cleaning contaminated water from metals.

FLUVIAL TRANSPORT OF C, N, P AND S BY VENEZUELAN RIVERS

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The Venezuelan rivers, that drain northward directly into the Caribean sea, have been selected to conduct a hydrogeochemical study with the main objetive of estimating the annual transport of C, N, P and S to the Caribbean sea. The Venezuelan Caribbean sea drainage basin has an area of 85,700 Km^2 and an annual runoff of 146 mm. The non-polluted and polluted rivers and streams draining different lithologies under different precipitation and runoff regimes have been monitored for C, N, P and S since 1987.

The transport of these elements has been fractionated by their source (natural vs. anthropogenic), form (dissolved vs. particulate) and chemical nature (inorganic vs. organic). The results obtained in this study indicate that the anthropogenic input excceds the natural input when the population density is greater than 200 persons/Km^2. The elements C, N and P are mainly transported as particulates while S is transported as dissolved. P and S are transported in their inorganic forms whereas C and N are transported in their organic forms.

The nitrogen and phosphorus especies more anthropogenically-influenced are the ammonium and the polyphosphates forms, respectively. Besides, the natural background concentration of S and P showed a strong dependency of the lithology drained.

The study has permitted to establish the baseline for all four elements as a function of lithology and runoff and to estimate the annual per capita input. This information is very useful when estimating the actual global fluxes of these elements into the sea.

SAMPLING AND ANALYTICAL QUALITY CONTROL (SAX) FOR IMPROVED ERROR ESTIMATION IN THE MEASUREMENT OF HEAVY METALS IN THE ENVIRONMENT, USING ROBUST ANALYSIS OF VARIANCE.

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The exact measurement of lead in the urban environment is limited by errors introduced by the sampling and analytical procedures. If these errors are not quantified, the spatial distribution of lead cannot be assumed to be that described by the chemical analyses.

Analytical quality control is routinely applied in environmental geochemical surveys in order to estimate the errors originating in the analytical procedures in the laboratory. The errors originating in the sampling procedures however, are not usually estimated systematically, although they are often larger than the analytical errors.

Sampling and Analytical Quality Control (SAX) extends the estimation of random error to include the process of field sampling. This is achieved by taking duplicate samples in the field separated by distances that reflect the uncertainty of the relocation of the site. These duplicate samples are treated as separate samples in the laboratory. Two analyses are made of both the field duplicates.

Analysis of variance (ANOVA) can be applied to seperate the random analytical and sampling error from the true variation of the lead concentration in the environment. Classical ANOVA is however very sensitive to a small proportion of outlying results. Experimental findings show that most environmental geochemical surveys have a few duplicates that are very discepant and these results are sometimes eliminated for that reason. The techniques of robust statistics, however, allows outlying values to be accomodated rather than rejected.

The new technique of Robust ANOVA has been applied to SAX data from two geochemical survey for lead. In a stream sediment survey of an area of Cornwall close to old lead workings, the combined processes of sampling and analysis accounted for only 4% of the total variance. Significant lead contamination can therefore be detected with certainty over the local background concentration. In a soil survey of a London park the combined sampling and anaytical variances accounted for 54% of the total variance. The observed dispersion patterns of lead in the park were therefore significantly distorted by the processes of measurement.

The combination of Robust ANOVA and SAX therefore measures the confidence that can be placed in the environmental interpretation made from geochemical surveys. Moreover, the comparison of the geochemical and measurement variances allows targets to be set for the precision of the measurement that is required to detect pollution of a given magnitude.

CHARACTERIZATION OF CURRENT GEOCHEMICAL PROCESSES IN FORESTED ACID SOILS USING THE TEST-MINERAL BAG TECHNIQUE.

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Anthropogenic effects such as acid rains were said to possibly dramatically change pedogenetic processes, especially podzolization. Such a statment supposes that the "undisturbed" current soil-forming processes were characterized. In an attempt to define the currently active geochemical processes in forested acid soils we adopted a qualitative experimental method in which a standard pure test-mineral (high CEC vermiculite) was inserted into the soil. Moreover the method was completed by introducing chelating or exchange resin bags into the soil.

Major geochemical processes operating in temperate acid soils were postulated to be either acidolysis by weak non-complex forming acids or acidocomplexolysis, i.e. reaction with complex forming organic acids (podzolization). We based the study on the following principles : when placed in an acidic and complexing medium the test-mineral undergoes a desaluminization process and its CEC saturates with Mg by relative accumulation. In a simply acidic system, aluminum accumulates in the interlayers, and rapid hydroxylation leads to the formation of an Al intergrade mineral easily detectable by X-ray diffraction. The resins inserted in soils should give information on the chemistry of the soil solutions.

Three sites were experimented : (1) Ardennes, a typical acid brown soil (Typic Dystrochrept); (2) Rambouillet, a well-drained podzol (Typic Haplortod) and (3) Médoc, an hydromorphic podzol (Typic Haplaquod). This results are for an experiment over 1 to 3 years, except the resin bags which stayed in the soils 1 year only.

For the three soils, the current geochemical process, as revealed by the test-mineral, was a weak acidolysis, even for the morphologically well-expressed podzols. In the well-drained podzol (Rambouillet), despite a rainfall close to the average (600mm/year) during the experiment, only the test-mineral or the resins in the most superficial (#< 15cm) horizons had reacted. We conclude that podzolization was not currently active in this soil because of a too low level of percolating water. In the hydromorphic podzol (Médoc), both the resins and the test-mineral had strongly reacted. But, although dissolved fulvic acids were present in the ground-water, indicating podzolization, that process was not revealed by the test-mineral. A possible explanation could be that in this soil the complexing ability of organic acids was reduced because of a low pH. Therefore podzolization in this soil would be mainly characterized by the translocation of organic compounds the complexing ability of which being too weak to prevent the accumulation of Al in the interlayers of the test-mineral.

PRELIMINARY RESULTS OF A STUDY OF QUALITY & NUTRIENT LEVELS IN SURFACE WATER AND GROUNDWATER, EAST OF LAKE THOMSON, JANDAKOT, WESTERN AUSTRALIA.

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ABSTRACT.

A study was carried out to look into the water chemistry of a large open drain and the surrounding groundwater, east of Lake Thomson at Jandakot. This area overlays the Jandakot groundwater mound, which is one of the two very important sources of water supply for the Perth Metropolitan Region. The main objectives of this study were to assess the nutrient loads in surface water and its relationship with groundwater chemistry.

Two large open surface drains in the study area eventually discharge into Lake Thomson. Surface water flowing through these main drains was monitored and analyzed for total phosphorus (TP) and total kjeldahl nitrogen (TKN) concentrations at 2 - 4 weekly intervals during the winter months in 1990.

"First flush" of surface water occurred in mid-May and drainwater analysis showed 'extreme' levels of TP and TKN (greater than 3.00 mg/L). This inability of 'flushing' may be attributed to shallow gradient and low volume of water in the drain. It was further complicated by uncleared vegetation and dead grasses within the drain causing stagnant pools. However, with increased drain flow a significant reduction of nutrients occurred but TP and TKN levels remained moderate to very high over wet winter period. This enabled the nutrient-responsive, free-floating fern *Azolla sp* to rapidly colonise the drain, completely covering the surface of drainwater. Large stands of bullrushes also grew indicating relatively high levels of phosphorus and nitrogen. During summer this vegetation decomposes within the drain and releases nutrients back into the drain. The highest calculated TP drainwater load of 460 gm/d occurred during mid-August simultaneously with the second highest calculated drainwater flow of 920 m^3/d. Nutrient loads in the drain appear to be directly related to the volume of water flowing through it. Agricultural sources are thought to be responsible for high nutrient loads in the open surface drains.

Groundwater was analysed for TP and TKN in Western Australian Water Authority observation bores. Analysis of groundwater from two shallow bores indicate high to very high TP and TKN levels. However, analysis of groundwater from four other deeper bores in general showed low to moderate levels of TP and TKN. This could be attributed to organic ferruginized sand layers, silts and clays underlying the Bassendean Sands acting as nutrient filters, thus removing a large proportion of excess nutrients that are leached down.

The shallow water table in the study area appears to be polluted with excess phosphorus and nitrogen concentrations which could seep into the drains that flow into Lake Thomson, thus increasing the nutrients in the lake.

CATION RELEASE DUE TO CHEMICAL WEATHERING OF SOIL MINERALS

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Impact of acid rain, and questions about the sustained fertility of unfertilized forest soils, have put focus on the kinetics of weathering of soil minerals, considering weathering to be the only essential source of proton buffering and many plant nutrients.

In order to investigate the weatherability, i.e. the kinetics of proton buffering and release of cations (calcium, magnesium, potassium, sodium, aluminium and iron) soil samples from eight locations were artificially weathered ≈eight months by use of sulfuric acid and EDTA (both at pH 3,0) as batch extractions including renewal of the extraction solution after suitable reaction times. The soils were from Ulborg, Lindet and Klosterhede, all poor and acid Danish sandy soils; from Trinderup (Denmark), Nordmoen (Norway) and Risfallet (Sweden), all relative rich sandy soils; from Sollingen, a German acid loamy soil; and from Stenholts Vang, a Danish relative rich loamy soil. From each profile a soil sample from an upper horizon (A or E) and one from a deeper horizon (BC or C) were used and separated in clay, silt and sand fractions. These fractions were used in the artificial weathering study.

Initially proton buffering were relative fast due to release of metal cations from relative reactive sites (exchangeable sites and amorphous oxides), but after few extractions the relative release rate (moles of metal release per moles of metal in the sample per time unit) became nearly constant (slowly declining over time) corresponding to a steady-state dissolution depending on the renewal rate of extraction solution. The relative release rate of the different metals varied among the samples (reflecting different mineralogical composition), the size fraction, and on the use of sulfuric acid or EDTA as weathering agent. Futhermore, additional consideration of composition (total metal content) and texture demonstrates even greater differences between the various soils both in proton buffering rate and in release rate of essential nutrient cations versus potentially toxic aluminium ions. The results are discussed in the light of soil development, and soil acidification versus increase in soil acidity.

EFFECTS OF HEAVY METALS POLLUTION ON SOIL-PLANT-ANIMAL SYSTEM IN SOME INFLUENCIAL ZONES OF POLYMETALLIC SULPHIDE PROCESSING

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ABSTRACT

The paper presents the research results on the effects on the heavy metals pollution on soil-plant-animal system in the influencial zones of the Turnu Măgurele Factory processing the Pyrite Ashes and the Aggregate Works for Chemical Fertilizers Valea Călugărească.

The airborne emissions looded with heavy metals and also deflation of fly ashe deposited in the spoil banks has as effect a looding of environment with heavy metals (Cu,Zn,Pb,Cd).

The Cu and Pb content of the soil was 2.6 and 1.7 times, respectively, higher than the maximum tolerable limits in soil. The alfalfa which grew around these factories contained 11 % more Cu than the threshold toxicity for plant nutrition and 7 times more than the threshold for sheep nutrition.

Chemical symptoms of sheep examinated, anatomo-pathological lesions at autopsy and analytical data of copper concentration in some organs and humours of sheep,in the influential zones of these factories, led to the conclusion that the animals presented a chronic copper intoxication state.

THE CLAMS OF THE COATZACOALCOS RIVER. IN THE MEXICAN SOUTHEAST AS INDICATORS OF POLLUTION.

THE INDUSTRIAL DEVELOPMENT OF THE STATE OF VERACRUZ HAS BEEN KEY FACTOR TO THE ECONOMY OF THE COUNTRY, SINCE MORE THAN FIFTY YEARS. MAINLY STRUCTURATE IN THE PETROLEUM INDUSTRY, THE PROGRES OF THE SOUTH OF THE STATE WAS NOT CONSIDERED THE AFECTION OF THE OWN TROPICAL ECOSYSTEMS OF THE REGION, GIVEN AS RESULT ACTUALLY, EXCESIVILY DEFORESTATION, DEMOGRAPHIC GROWING, RIVER AND LAGOONS POLLUTED, DRIED SWAMPS THAT HAVE BEEN USED AS-RECEPTORS.
A CHARACTERISTIC CASE OF THE ECOLOGYCAL PROBLEM IN THE SOUTH OF THE VERACRUZ THAT IS THE COATZACOALCOS RIVER. RECEIVING DAILY TONS OF INDUSTRIAL AND MUNICIPAL WASTES IN MORE THAN A HUNDRED OF VARITIES, THE COATZACOALCOS RIVER IS THE NATURAL HABITAT OF ORGANISMS THAT HAVE RESISTED OR HAS BEEN ADAPTED TO A DETERIORED ENVIRONMENT FOR THE ANTROPOGENICS ACTIVITIES. BEING THE CLAMS SESSILES ORGANISMS AND CAN BE LOCATED ALONG THE RIVER WHICH ARE USED IN THIS RESEARCH AS INDICATORS OF POLLUTION.
THE OBJECTIVES ARE: THE TAXONOMIC IDENTIFICATION OF THE CLAMS OF THE COATZACOALCOS RIVER FROM ITS MOUTH TO THE SEA, APPROXIMATELY SIXTY KILOMETERS INTO UP RIVER; DETERMINATION OF THE CONCENTRATION OF HEAVY METALS, HYDROCARBONS AND COLIFORMS BACTERIES IN SAMPLES OF CLAMS OF THE SAME AREA; DETERMINATION OF THE COLIFORMS BACTERIES IN THE WATER OF THE SAME AREA; DETERMINATION OF THE GRADE POLLUTION OF THE COATZACOALCOS RIVER CONSIDERING THE CLAMS AS INDICATORES OF THE POLLUTION.
THE MONITORING THAT TAKES PLACE ALONG SIXTY KILOMETERS OF THE COATZACOALCOS RIVER, BEGINNING FROM THE MOUTH OF THE GULF OF MEXICO APPROXIMATELY EACH FIVE KILOMETERS, DEPENDING OR NOT OF THE EXISTANCE OF THE MOLLUSC. THE MONITORING TAKES PLACE IN DIFERENTS STAGES OF THE YEAR.
THE HEAVY METALS WERE DETERMINATED CUANTITATIVELY BY ABSORTION ATOMIC SPECTROPHOTOMETRY. THE HYDROCARBONS BY CHROMATOGRAPHIC METHODS AND THE COLIFORMS BACTERIES BY THE NMP METHOD.
THE REACH OF THE EFECTS OF THE POLLUTION IN THE COATZACOALCOS RIVER HAVE BEEN CLEARLY OBSERVED IN THESE STUDIES. THE CONCENTRATION OF THE ANALIZED POLLUTANTS IN THE CLAMS IS HIGH, KEEPING SIMILARITY IN ALL THE MONITORED ZONE. IN THIS STUDY MERGED THE NEED OF THE STABLISHMENT OF PROGRAMS OF MONITORING FOR THE CONSTANT DETERMINATION OF THE ECOLOGYCAL CHANGES. THIS THROUGH AQUATIC ORGANISMS, SUCH AS THE FOUR CLAMS FOUNDED IN THE COATZACOALCOS RIVER THROUGHOUT THIS RESEARCH.

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GEOCHEMICAL MODELING TO PREDICT THE CHEMISTRY OF LEACHATES FROM ALKALINE SOLID WASTES

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Abstract

Oil shale deposits in the western United States contain mainly kerogen and carbonate minerals. Oil is recovered from the shale by thermally decomposing the kerogen at elevated temperatures, which results in production of large amounts of alkaline oil shale solid wastes (OSSW). One of the major environmental issues associated with the disposal of OSSW is prediction of the behavior of potentially toxic chemicals in the OSSW disposal environment. The objective of this study was to use a geochemical code to help predict the chemistry of leachates, including toxic chemicals, from OSSW. Several geochemical codes were evaluated (e.g., MINTEQA2, WATEQFC, EQ3/EQ6 AND GEOCHEM) and the code GEOCHEM was selected based on its more comprehensive capabilities. Three OSSW's were subjected to solubility and X-ray diffraction studies. Total elemental concentrations and pH of leachates from the OSSW's were used as input to the GEOCHEM code to predict their chemistry. The ion activity products were used to infer the likely solid phases controlling the concentration of toxic chemicals (F and Mo) in leachates. The model predicted that silicate phases produced during the heating process initially buffered the pH and controlled concentrations of major cations. The F^- concentrations in OSSW leachates suggested a close saturation with respect to fluorite (CaF_2). Furthermore, contrary to previous findings, GEOCHEM predicted that powellite ($CaMoO_4$) probably does not control the concentrations of Mo in OSSW leachates. A discussion of the advantages and disadvantages of using existing geochemical models to predict the chemistry of leachates from OSSW will also be presented as part of this paper.

GEOCHEMICAL SPECIATION AS RELATED TO THE LEACHING OF TOXIC ELEMENTS IN THE VADOSE ZONE OF A CALCAREOUS SOIL

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Abstract

Alkaline conditions often enhance solubility and mobility of anionic toxic elements in calcareous soils. The objective of this study was to examine chemical speciation to evaluate potential solid phases controlling the concentrations of F, Mo and Se and thereby predict their mobility at various depths in the vadose zone of a calcareous soil. Pore waters of soils were extracted with distilled-deionized H_2O by reacting for 7 and 14 days(d) at 25 ± 0.5°C. Soil leachates (filtrates) were measured for pH, total concentration of cations, anions and trace elements. From total elemental concentrations, ion activities and solution species (ion complexes and ion pairs) were calculated using GEOCHEM speciation model. From ion activities, ion activity products (IAPs) were calculated and compared with solubility products (K_{sp}s) to determine potential solid phases controlling the solubility of F, Mo and Se. As depth of the soil increased (0-70 cm), the pH increased slightly (from 7.95 to 8.12) and concentrations of F (from 0.77 to 6.74 mg L^{-1}), and Mo (from 0.06 to 0.15 mg L^{-1}) also increased. The Se concentration increased slightly (from 0.002 to 0.005 mg L^{-1}) and it also showed higher levels at intermediate soil depths. Chemical speciation of leachates suggested that total fluorine was dominated by the free F^- ion. Total molybdenum existed as $MgMoO^\circ_4$ followed by $CaMoO^\circ_4$ and MoO_4^{2-}. For Se, $MgSeO_3^\circ$ species dominated soil leachates, followed by SeO_3^{2-}, $CaSeO_3^\circ$ and SeO_4^{2-} species. A comparison between IAPs and K_{sp}s for different solid phases suggested that F, Mo and Se concentrations in the vadose zone of these soils may be controlled by CaF_2, $PbMoO_4$, and Cu_2Se, respectively. Results suggest that leaching of F, Mo and Se in the vadose zone of calcareous soil is related to the increase in pH and the chemical form of the element present in the pore waters of soil.

ADVANCED GEOCHEMICAL SPECIATION - A TOOL READY FOR ENVIRONMENTAL IMPACT ASSESSMENT?

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Abstract

The study of the emission and distribution of hazarduous pollutants, released from a variety of human (industrial) activities, and the difficulties arising from the translation of measureable effects into applicable and economically acceptable solutions for decision-making and remedial measures requires a good net-work of communication and exchange of information as well as coordination between scientists, engineers and all responsible authorities involved at different levels.

Probably we can not avoid, that our use of the earth's resources (air, water, soil, food, energy) will always provoke some kind of perturbation in the environment. All human activities interfer and modulate the natural occurence and cycling of elements increasing or lowering elemental fluxes within **primary** (weathering, leaching, mineralization) and **secondary** processes (photosynthesis and metabolisms within living matter). Man's participation and involvement into biogeochemical processes can lead to the (1) enrichment, (2) depletion and/or (3) substitution of both essential, indifferent and toxic elements removing naturally evolved and maintained steady-state systems by shortterm and unmatured sub-systems which are characterized by a low physico-chemical stability.

Today, in many highly industrialized countries the performance of environmental and health **risk** assessments has become an obligation for all kind of enterprises (projects, plants, procedures) which may give rise for severe adverse effects. For this, the respective industrial or public companies planning this type of operation are asked by controlling and authorizing agencies in an early stage to demonstrate that the risk for human and environmental health will not increase and that any effect caused by the planned activity or program will remain within the officially established and scientifically accepted limits. The basic idea behind this is to quantitatively identify all direct and indirect effects **in advance** so that it will be possible to prevent, minimize or mitigate any harm which may be induced by the planned measures.

With regard to **activities**, like (i) resources extraction and recovery, (ii) industrial production and use, (iii) energy generation and consumption and (iv) waste disposal, this type of **examining approach** requires **geochemical** expertise. In order to get an estimate of the natural preload, sensitivity and tolerance of the area in concern, geochemical monitoring before, during and after the planned operation may assist and safeguard the project design and performance by the early detection of any disturbances of the original elemental cycling. In this context, the **chemical speciation** of substances released to the environment, e.g. raw materials extracted (chemicals, minerals, water, fuels), industrial products (technical and consumary compounds) and waste material (fly ash, gases, sewage, sludge), by specific analytical and instrumental techniques (like chromatographic and spectrometric methods), which are able to separate and detect physico-chemically similar compounds in a distinct environmental sample as an elemental or molecular configuration, may help to anticipate and determine the potentially **conflicting situation** between site-specific and highly vulnerable targets and pathways and the possible transformations and final impact of particular pollutants.

OVERBANK SEDIMENTS IN STUDIES OF POLLUTION FROM MODERN AND HISTORIC MINING

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Overbank sampling methods have, in recent years been suggested as a suitable means both for regional scale geochemical mapping and for differentiation between pre-anthropogenic and post-anthropogenic levels of trace elements in the environment. The application of this technique is discussed in the context of semi-arid terrain in central Mexico, with the specific aim of identifying anthropogenic introduction of metals into the local environment from mining practices.

Initially, sampling was conducted in the basins of the Guanajuato and Laja rivers, two catchments which are of similar lithological character, but with the former having a long history of metallic mining and processing. Profile sampling of vertical sections through floodplain sediment sequences was undertaken and the -150µm size fraction analysed by XRF spectroscopy for a range of major, minor and trace elements including many with implications for animal and human health . Active stream sediments were also collected to allow comparison of the geochemical patterns exhibited by an alternative sample medium in this terrain. A second phase of sampling has been conducted in basins draining different lithologies which may be expected to demonstrate widely differing geochemical characteristics. Again, one of the catchments drains an area of historical and active mining.

Field identification of discrete units within the overbank profile proved straightforward, and in some cases specific marker horizons could be traced between profiles enabling relative ages to be assigned. In addition, many artifacts of 'modern' society were found in the upper parts of profiles clearly indicating recent deposition of the floodplain sediment. The geochemical data obtained do not however show clear systematic variation through the profiles and do not provide conclusive evidence of gross metallic pollution from mining operations.In general there is little obvious difference between pre- and post-anthropogenic levels of potentially toxic metals in the areas studied, although minor contamination events can be identified in some horizons. Of particular interest are occasional horizons showing strong enrichment of arsenic (and some associated ore metals).

Stream sediment geochemistry typically shows a clear similarity to the most recently deposited floodplain material and in no cases is strongly suggestive of any mining related pollution. Both sample media identify lithogeochemical characteristics of the region which may be of some significance in agricultural applications, notably very low levels of the essential elements copper, zinc and cobalt.

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CHEMICAL DENUDATION IN BARUUN-BAYAN-GOL DRAINAGE BASIN (KHENTEY MTS.,MONGOLIA)

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Khentey Mts. located in northern part of Mongolia are drained by tributaries of Selenga river which swells Baikal Lake as well as tributaries of Amur river falling into Pacific Ocean. The mountains of maximum height 2731 m a.s.l. are characterized by extremly continental climate. Annual precipitation varies from 200 to 300 mm and temperature amplitude is over 80^{0}. In the period from June until August 80 % of annual precipitation falls down. Winter period is almost snow-free. The entire mountain ridge is located in the zone of permafrost. Hydrological regimes of Khentey rivers are very complex. Small and medium rivers are frozen down to bottoms during 5-6 months. Spring flood is due to thawing of aufeis (naleds) and therefore is moderate while summer flood caused by rains is much larger. Ground water beneath permafrost and water coming from active layer thawing in summer contribute to river flow. Vegetation cover - mountain steppe - favours surface runoff and taiga terrains are very moist. The most important, and sometimes the only one way of transportation of weathering products out of the drainage basin is transporatation as solutions.

Studies on mineralizaton of water (using field conductometer) in Baruun-bayan-gol drainage basin were carried out in July of 1989 and 1990. In previous years, detailed investigations on mineralization and chemical composition of water were performed in Dunda-baydalagiyn-gol drainage basin which is located in the same region and which geology is identaical (granites, metamorphic shales, quartzites). Ions HCO_3^- and Ca^{2+} are predominant in chemical composition of river water. Spring water is characterized by significant amounts of the following ions : Cl^+, Na^+, Mg^{2+} and SiO_2. Minaralization of water of Baruun-bayan-gol drainage basin is very low, less than 50 mg/l and ca.100 mg/l in river water. Ground water, particularly that of deep circulation, is characterized by mineralization of the order of 200 - 300 mg/l however, participation of that water in river runoff is practically meaningless in summer. Very strong correlation between mineralization of water and geological structure and elevation above sea has been stated. Water of smallest mineralization are found in the uppermost parts of drainage basin and in the areas where metamorphic shales occur. Contents of isotopes are as follows: in the case of ^{18}O it varies from -9.8 to -13.3, $^{13}C_{PDB}$ it is - 14.7 to 19.3 in summer. Rate of chemical denudation in Selenga drainage basin is ca. 10 tons/year per $1km^2$ while in Baruun-bayan-gol drainage basin is likely smaller and does not exceed 3 tons/year per 1 km^2.

ACIDIFICATION AND WEATHERING OF PODZOLS IN THE MONTSHEGORSK AREA, KOLA PENINSULA AND IN EASTERN FINNISH LAPLAND

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The dieback forest in the surroundings of the Montshegorsk smelting plants and the decline of pine forests in eastern Finnish Lapland led to a co-operating project including the Kola Scientific Center and the Geological Survey of Finland in 1989. The purpose of the research is to investigate the natural soil acidification and weathering rates of podzols in relation to the anthropogenic acidification. The present paper introduces the preliminary results of the program eastern Finnish Lapland.

As a total 11 profiles of humus and podzols of glacial drift were sampled from two test areas of the dieback forest near Montshegorsk and from two less polluted forests in the Apatity-Kirovsk region in Kola Peninsula in summer 1989. In all 22 profiles of podzolized drift in northeastern Finnish Lapland were sampled from seriously to slightly damaged forests area at Naruskajärvi and in the Ivalo-Inari area in the same summer.

The concentrations of 9 elements of the easily leachable fraction from the air-dried humus samples were analyzed with the buffered NH_4-acetate method (pH 4.5), and concentrations of 31 elements by ICP from the ashed humus samples with the hot aqua regia digestion.

The fraction < 0.5 mm was sieved from air-dried mineral soil samples. The solubility of Al and the base cations Ca, Mg, K, Na, and pH were measured with the acid neutralizing capacity (ANC) method, which includes a dilute NH_4NO_3 and two acidic NH_4NO_3 extractions. The hot aqua regia digestion was used for measuring the element composition of the micas and clay minerals. The mineral identification of silt and clay fractions was made with the X-ray diffraction method including the acidic ANC-extraction and heating treatments.

The buffering capacity of mineral soils of the Archaean granite gneiss area will be exhausted within a short period of time due to a low concentration of mineral nutrients, and saprolite containing drift rich in Al and Fe. Aluminium buffering reactions dominantly neutralize the extra acid load in mineral soils of the studied test areas. The anthropogenic acidification in the dieback forests of Montshegorsk seems to cause a lability of clay mineral structures. The superabundance of Al precipitates in some of the test profiles of the dieback forests are associated with the more intensive mica and plagioclase weathering from the fine fraction of drift than in areas of lower acid deposition. Humus layers in the Montshegorsk area were impoverished in mineral nutrients Ca and K and strongly enriched in such toxic elements as Al, Ni, Cu, Cr, As and Cd.

DISTRIBUTION OF TOXIC TRACE ELEMENTS AND NUTRIENTS IN THE SEDIMENT OF LAKE BREITLING - ASPECTS OF THE RELATIONSHIP BETWEEN FRESH WATER AND SEDIMENT QUALITY.

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The glacial lakes updown of the urban district of Berlin are of great importance for industry, drinking water supply, traffic, agricultural and spare time activities of about 5 million people in this region.

Inadequate waste water treatment has dramaticaly increased the trophic state of the lakes during the last decades. A wide range of environmental chemicals have been accumulated in the sediments with a disastrous effect on benthic fauna.

The paper presents results on the distribution of toxic trace elements in the sediment of lake Breitling (600 ha) and a discussion of nutrient remoblisation from sediment. The < 185 µm fractions of 600 freeze dried single samples of 21 short-cores and one 14 meter-core have been analysed by x-ray diffractometrie, ICP-AES, AAS and other methods.

The P content of sediment steadily has decreased from 3000 BC up to the last century. The C/P quotient is lower than those of algea biomass in deeper parts of the core (25), reflecting a efficient P fixation and C loss, caused by the bacterial biomass decomposition. C/P increases up to 220 for a paleo-lake depth of 5 m, indicating more than 80 % P remobilisation.

The carbonate content has decreased with rising sediment top in result of calcite resolution by more extensive aerobe decomposition of settled organic material during lake evolution. Calcite and P have increased again with rising sedimentation rates (up to 4 cm) in last decades. Beside of increased nutrient input the P rise may reflect a hindrance of P remobilisation by more rapid settling of new particulated material.

Fe-oxide, -hydroxide species play a dominant role for P fixation in sediments of Havel lakes. We have found high P contents, coincidencing with higher Fe contents in influx regions of lake Breitling. Ferroussulphide formation in sediments competes with P fixation for Fe inventory. Only 10 % of total Fe inventory are sulfidic bounded in deeper sediment, while it are 75 % in recent sediment.

Attemps to reduce the eutrophic state of the shallow Havel lakes by lowering the nutrient input have to consider the dynamic of P exchange between water and sediment. Up to now fixed P may be remobilised to act counterproductive if the sedimentation rate decreases.

A nearly constant heavy metal content on high level within

the upper 25 to 50 cm sediment (depending on various sedimentation rates in different parts of the lake) could be observed.

The enrichment factors with reference to the geological background for selected toxic trace elements within the upper 9 cm sediment increase in the following order (increased clay mineral input was considered for background): Co(1), Be(1), V(1.1), Se(2.8), Bi(7), Pb(13), Cu(14),Cd(259, Zn(500).

The enrichment seems to be higher than 20 for As and 10 for Tl (both elements could not be detected in the deeper parts of the 14 m-core).

FÖRSTNER et al. (1989) propose to multiplicate the enrichment factors with such for toxicity to get ecological risk indices (e.r.is.) for single heavy metals. The following e.r.is. of the surface sediment of lake Breitling result by using this approach: Zn(x5) 250, Cd(x10) 250, Cu(x5) 70, Pb(x1) 13. In comparison to e.r.is. to strongly polluted German river sediments the high e.r.i. for Zn is remarkable. Additional we have found, that in opposite to Pb and Cd a high percentage of total Zn (5.6 %) can be leached with 1 M NH4Ac solution.

The relations between physical and chemical site properties in a series of Norway Spruce stands with various degrees of waterlogging

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Waterlogged soils are widespread in mountainous areas of Central Europe which have developed on clay chists or solifluctional slope sediment soils. Exess water in such soil profiles causes mottled horizons that largely differ in their soil chemical characteristics from well drained horizons. The rooting pattern of Norway Spruce matches these vertical gradients in physical and chemical properties. Where waterlogging occurs close to the surface of the mineral soil, older stands experience an increased risk of large scale collaps by strong winds. These sites generally have a high potential of productivity, but suffer from the risk imposed especially by winds. Thus the management of such sites depends on a realistic assessment of these risks.

The processes that may have caused the physical and chemical site characteristics are:

- development of the natural soil structure due to rooting and aggregation
- secondary compaction due to conversion from decidious into conifer stands
- secondary compaction from management practises such as heavy trucks, clearcutting with extended periods of low water-consumption by the vegetation
- chemical changes due to conversing site species
- chemical changes due to increased atmospheric deposition
- differences in the silicate weathering from the parent material in the various soil layers

These processes act on different time scales ranging from several centuries to an event-type. This paper gives
a) an inventory on the current state of different dynamic and static physical and chemical variables (water potentials, water retension curves, CEC, base saturation, water extracts)
b) it shows that the current chemical state can be explained by the hydrological dynamics, which have been simulated by a two-dimensional distributed flow model (Hauhs 1985)
c) two ecosystem-scale szenarios showing how these variables may be linked through soil acidification and compaction.

FLUVIAL TRANSPORT OF C, N, P AND S BY VENEZUELAN RIVERS

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The Venezuelan rivers, that drain northward directly into the Caribean sea, have been selected to conduct a hydrogeochemical study with the main objetive of estimating the annual transport of C, N, P and S to the Caribbean sea. The Venezuelan Caribbean sea drainage basin has an area of 85,700 Km^2 and an annual runoff of 146 mm. The non-polluted and polluted rivers and streams draining different lithologies under different precipitation and runoff regimes have been monitored for C, N, P and S since 1987.

The transport of these elements has been fractionated by their source (natural vs. anthropogenic), form (dissolved vs. particulate) and chemical nature (inorganic vs. organic). The results obtained in this study indicate that the anthropogenic input excceds the natural input when the population density is greater than 200 persons/Km^2. The elements C, N and P are mainly transported as particulates while S is transported as dissolved. P and S are transported in their inorganic forms whereas C and N are transported in their organic forms.

The nitrogen and phosphorus especies more anthropogenically-influenced are the ammonium and the polyphosphates forms, respectively. Besides, the natural background concentration of S and P showed a strong dependency of the lithology drained.

The study has permitted to establish the baseline for all four elements as a function of lithology and runoff and to estimate the annual per capita input. This information is very useful when estimating the actual global fluxes of these elements into the sea.

Transport of Reactive Solutes in Soils; A Simplified Approach

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ABSTRACT

Solute retention and mobility in porous media plays a significant role in their leaching losses beyond the soil rootzone and the potential contamination of groundwater supplies. The ability to describe the transport of solutes in porous media is essential for accurate prediction of chemical fluxes and quantifying hazardous waste transport. To predict the transport of reactive solutes in porous media, models that include retention and release reactions with the soil matrix are needed. Retention and release reactions in soils include ion exchange, adsorption/desorption, precipitation/dissolution, and other mechanisms such as chemical or biological transformations.

A simplified multicomponent model was developed for the purpose of predicting the transport and retention of reactive solutes in soils. The basis for this approach is that two reaction mechanisms of solutes in the soil solution are assumed to be the dominant retention processes in the soil system. These retention mechanisms are the adsorption/desorption of ion exchange reactions and that of the specific sorption mechanisms. We consider ion exchange as an instantaneous reaction representing non-specific sorption mechanisms and as a fully reversible reaction of ions in soil solution and that retained on exchange sites of the soil matrix. In contrast, specific sorption was

considered as a kinetic process of the second-order type. Specific sorption was assumed to represent retention of ions with strong affinity for specific sites on matrix surfaces. Furthermore, retention of ions via specific sorption was regarded as an irreversible or weakly reversible process. Moreover, the assumption of local equilibrium for the ion exchange reaction was relaxed and a fully kinetic model was developed. The proposed kinetic ion-exchange reaction was analogous to mass transfer or diffusion between the solid and solution phase. The two solute retention approaches were incorporated into the dispersion-convection equation and model sensitivities were performed.

To illustrate the capability of the model in predicting the transport of a reactive solute in porous media, we examine model description of experimental results for two data sets. The data sets are measured miscible displacement results for Cd transport in uniformly packed columns of Windsor sandy loam soil and Eustis very fine sandy soil. For Windsor soil, the use of small values for the kinetic ion exchange parameter provided improved prediction of the observed breakthrough results. However, incorporation of ion exchange with specific sorption best described effluent Cd concentration in this soil. For Eustis soil, a pronounced chromatographic effect was observed which is primarily due to changes in the total concentration of input pulse solutions. Here the measured peak concentration was about 5 folds that of the input Cd pulse. Moreover, the use of the simplified approach with the assumption of local equilibrium predicted adequately the shape and location of the breakthrough results for Eustis soil. However, apparent Cd retardation was overpredicted in comparison to observed measurements.

THE EFFECT OF NON-FICKIAN TRANSPORT ON SORPTION KINETICS

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Contaminant transport in aquifers is a result of hydrodynamic and (bio)chemical processes that often interact under highly heterogeneous conditions. Preferential flow paths, or non-Fickian effects, are typical phenomena in such aquifers. On the field scale, equilibrium and non-equilibrium sorption-desorption are believed to describe well a large number of the (bio)chemical reactions of interest. Moreover, sorption kinetics incorprates physical non-equilibrium effects due to solute diffusion into essentially immobile (low conductivity) zones.

By convoluting an analytical solution for sorption-desorption with travel times of advecting solute particles an efficient method for incorporating sorption kinetics into particle tracking models is first proposed. A Monte Carlo approach is adopted, and the heterogeneity in hydraulic conductivity is modeled using a stochastic turning bands method. The flow is mainly horizontal due to the subjected boundary conditions and the breakthrough of solute is calculated at vertical planes. Using this method, the influence of highly variable flow on sorption kinetics is investigated.

The resulting non-equilibrium breakthrough curves converge to the two limiting cases of equilibrium transport with retardation factors equal to one and two when the sorption and desorption coefficients approach zero and infinity, respectively. If the sorption and desorption coefficients are equal then the range where non-equilibrium effects will be important can be determined by the product of the sorption coefficient and the mean arrival time of a conservative solute. The results furthermore indicate that non-equilibrium effects have a stronger influence under conditions of low heterogeneity and anisotropy, whereas for high spatial variability and anisotropy in hydraulic conductivity the effects are to a certain degree lost in the spreading caused by the non-Fickian transport. The error one introduces by assuming equilibrium reactions with a retardation factor equal to two is thus smaller for highly heterogeneous formations than for more homogeneous ones; the first solute arrival is underestimated, however, when this assumption is used. Since both non-Fickian transport and sorption kinetics imply higher spreading of the solute these two effects can be hard to distinguish on the field scale. The second temporal moment of the arrival time can, however, be used as a means to estimate which process or processes that are governing a certain transport situation. The shape of the moment vs. distance curve generally provides information on whether the flow is Fickian or non-Fickian, whereas the moment calculated at different mass fractions at a constant distance can provide information on whether sorption kinetics influence the transport. This information may have important implications, for instance, when designing tracer tests for estimating the sorption parameters in highly heterogeneous formations.

MOBILITY OF MERCURY IN AQUATIC ENVIRONMENTS OF PANTANAL, BRAZIL: I. CARACTERIZATION OF ENVIRONMENTS.

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This work was developed in Pantanal, municipality of Poconé, Mato Grosso state, Brazil.

With the purpose of characterize the aquatic environments of the Pantanal, we have elected seven ecologic micro-environments to be monitorized, once they were understood to represent the regional ecosystems. These are seven lakes of naturalor anthropogenics origins.

There has been done monthly analysis of the following physicochemical parameters during a period of 9 months (from jun,1990 to feb,1991): pH, Eh, condutivity, total alcalinity, total hardness, total iron, oxicline, thermocline and phosphorus.

The bottom sediments of each environment was sampled with 45 cm of depth, and was analized at intervals of 5 cm for carbon, sulphur and total mercury contents. Analysis of a-clorophyle, BDO, CDO and X-ray of clay minerals was realized.

Related to biota systems, analysis in macrophytes, mollusks and fishes from contamined and uncontamined places were realized. Simulations on laboratory was realized to help to understand the incorporation mechanisms.

The results show that in most time of the year (seasonality) the physico-chemical condictions are not propicuous to oxidation and solubilization of mercury.

The contamination levels found in organisms are below of expected, denoting the rate of methylation is low in this region.

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COMBINED STUDIES OF SOIL AND GROUNDWATER CHEMISTRY IN HALLAND, SW SWEDEN

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Soil and groundwater samples are comparatively studied at twelve sites in Halland, consisting of 2 wells installed in quaternary deposits and 10 springs. These sites are participating in a groundwater acidification monitoring programme. The overall objective of the project is to be able to predict local trends in groundwater quality (i.e. health aspects) and soil status in the future based on different environmental impact scenarios (i.e. acid deposition). At each site, soil has been sampled from the A, B and C soil horizons in 3-5 excavations upgradient the spring/well. The soil chemistry is interpreted and discussed parallel with the chemistry in groundwater. The mineralogy of selected soil samples is studied by X-ray diffraction (XRD), which give an idea about weathering features. On the basis of groundwater data and analytical results for the soil samples, available computer models will be used for estimations of weathering rates and groundwater-soil mineral equilibria.

Preliminary results indicate a relationship between various chemical parameters in groundwater and the exchangeable acidity in the C horizon. Variations in the mineral composition within the clay mineral fraction (< 2um) seem to be present, but quartz, feldspars and clay minerals dominate in general. The most abundant clay minerals are chlorite-vermiculite and illite, which show variable proportions in the samples studied. This indicates the differential weathering of some samples.

NATURAL CARBONATE-BASED FERTILIZERS IN THE KRAKÓW-KATOWICE AREA, S POLAND

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A serious ecological threat exists in some parts of southern Poland, particularly close to big urban and industrial centers of Kraków and Katowice. This area, 4.1% of the Polish territory, forms a hub of our industry, including coal, zinc and lead mines, coal processing and base metal plants, chemical factories and steel mills (two biggest ones in Poland are localized there). Power stations and central heating facilities burn hard coal which is mostly high in pyrite. Under such conditions rains are acid and their impact is aggravated by other atmospheric pollutants: close to 40% of gaseous and dust emissions in Poland originate there. There is an urgent need to provide population with a "clean food" and healthy recreation centers (sport grounds, gardening sites etc.). Urban and industrial emissions must be scaled down but steps should also be taken to improve the devastated environment. Significant tracts of productive land have already been degraded in the Kraków-Silesia region by the human activities, thus agrotechnical parameters of soils there should be immediately rehabilitated. A wide use of natural carbonate fertilizers could be quickly implemented as carbonate rocks are abundant in the area, estimated at 80% of domestic reserves of dólomites and 5% of limestones.

Almost 520 occurrences of such rocks were recorded in the region, then their mineral composition, structural and textural features investigated and selected elements analysed for (MgO, CaO, Zn, Pb, Cd). Laboratory tests were carried out on the most promisive rock types regarding their role in sorption and desorption of heavy metals. However, the best results were obtained with mixtures of dolomites and clay rocks. Dolomites not only increase pH of soil solutions but also yield Mg and Ca ions. Clay minerals, particularly their modified varieties, provide valuable macro- and micro-bioelements, present on their exchange positions or attached to active structural centers. Clay minerals may also block heavy metals, falling with industrial emissions, neutralizing them as hardly soluble hydroxy-metal complexes. Next two maps of the scale 1:100,000 were drawn, showing occurrences of agriculturally suitable carbonate rocks. As an addition, a computerized data base was created for any IBM-compatible computer with basic peripherals. The base can easily be extended with the progress of exploration and analytical works. Our idea is to establish a pool of ecological information for local authorities. Considering current political changes in Poland it is at this local level that vital planning and policy-making will be delegated.

GEOCHEMICAL MARKERS OF CONTINENTAL PALAEO-ENVIRONMENTS. RELATIONS BETWEEN CLIMATIC CHANGES, VEGETATION AND GEOCHEMISTRY OF LAKE SEDIMENTS IN SOUTH BRAZIL

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The reconstitution of continental palaeo-environments of recent periods is generally based upon the study of bio-markers such as pollens, ostracods, diatoms,... or of isotopic markers (^{13}C, ^{18}O, ^{2}H). The use of those markers is however not always possible because of various limitations in their practicability: time for acquisition, cost, lack in collected material. On another hand, one can assume that climatic changes have induced variations on mobilization of chemical elements since weathering strength, complexation by and nature of organic ligands, kinetic of erosion are greatly dependent, directly or indirectly through induced vegetation, on climatic factors. The aim of this paper is to discuss the possible use of geochemical parameters for the evaluation of climatic changes during the Quaternary.

The results are based on the study of a 6-meter deep lacustrine drilling near the Salitre (Ti, REE) lateritic deposit in southern Brazil. The pollen analysis of the sediments shows up seven palaeoclimatic zones based upon the changes in tree pollens percentages during the last 30,000 years. Regression and development of the forest point out a succession of humid and dryer conditions through the variation of the length of the dry season. Furthermore the nature of the forest indicates variations of the mean annual winter temperature, revealing especially a cold and moist climate between ± 9,500 and 6,500 years B.P.

The chemical analysis of the sediment samples was performed for the major and trace elements, including rare earth elements. The results show a perfect correlation between the non-detritic SiO_2 content and the percentage of arboreal pollens: this content increases when (rain)forest dominates. This can be interpreted as the result of maximum lixiviation and transport of silica under rainy climate with subsequent accumulation in the sedimentation basin. The same behaviour appears for the Ce/Eu ratio which is high during forest stages but diminishes during the regression phase. This parameter could reflect higher inflow of reducing organic matter in soils leading to enhanced outflow of reduced Ce^{3+} in the drainage system. During the younger forest period (9,500 y B.P. - 5,500 y B.P.), the La/Yb ratio, expressing REE fractionation, presents a drastic depletion which can be explained by a greater complexation of heavy REE relative to light ones or by more acid conditions during this period. This is entirely compatible with the particular coniferous forest (Araucaria forest) found at this time.

All these observations are positive arguments for the use of geochemical markers as an aid in the reconstruction of climatic changes.

SOIL EXCHANGEABLE CHEMISTRY AND ACIDITY AT INTEGRATED MONITORING SITES IN FINLAND

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Soil exchangeable chemistry and acidity data are presented for 18 permanent plots sited in four coniferous forested catchments situated in background pollution areas in southern, eastern and northern Finland. The catchments and research form the Finnish contribution to the UN-ECE Pilot Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems, the overall aim of which is to monitor and model the effects of long-range transported air pollution on the state of ecosystems. In our presentation, we aim to describe the concentrations and pools of relevant soil acidification parameters presently encountered in the plots and to quantify the amounts of within- and between-plot, and between-catchment variation. Sampling and analyses follow the guide-lines given by the pilot programme. The samples were taken in 1988-89 and the soils were podzols or podzolised. Some plot average values were as follows. pH (water) ranged from 3.51 to 4.09 in the surface organic (humus) layer, and from 4.12 to 4.61 and from 4.50 to 5.42 in the 0-5 cm and 5-20 cm mineral soil layers, respectively. Effective cation exchange capacities in me/kg oven dry soil and me/m^2 per layer (in parentheses) were: humus, 207-332 (619-2211); 0-5 cm, 10-48 (605-2132); and 5-20 cm, 3-26 (561-4102). The range of base saturation values for the same layers were: 68-87 %; 15-42 %; and 21-49 %. Ranges of exchangeable Al^{3+} pools (me/m^2) in the corresponding layers were: 0-142, 337-1108, and 150-2488, and accounted for 0-39 %, 58-86 % and 50-83 % of the exchangeable acidity in each layer, respectively. The Ca/Al molar ratio in the mineral soil layers averaged between 0.2 and 1.3 (0-5 cm) and between 0.3 and 1.8 (5-20 cm). The amount of organic matter was very important in determining the exchange and acidity chemistries of these soils.

THE LINK BETWEEN SULPHATE ADSORPTION, SOIL PARENT MATERIAL AND SOIL pH IN SCOTLAND

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Sulphate adsorption in soils has attracted considerable attention over recent years, because of the buffering effect it temporarily has against soil acidification in response to acid deposition. Sulphate adsorption leads to base cation retention on soil cation exchange sites, whereas sulphate saturation results in base cation leaching and a reduction in soil pH. It is important therefore to include soil sulphate adsorption characteristics of soils when assessing short- to mid-term impacts of sulphur dioxide and sulphuric acid deposition on a regional scale. A method is therefore needed which allows mapping of predicted sulphate adsorption effects at reasonable cost.

Several approaches to solving this problem have been investigated by the authors. The most fruitful have been those which depend upon changes in sulphate adsorption with depth in the soil profile, particularly in soil B horizons. An initial survey strongly suggests that sulphate adsorption capacity is controlled primarily by the nature of soil parent materials, because of their effect upon the amounts of amorphous iron and aluminium hydrous oxides produced in soils. The degree of sulphate saturation, however, varies with pollution load at a given site. The relationship between this observation and the critical loads maps prepared for the UK, and Scotland in particular, will be discussed. The significance of the study to soil and freshwater acidification will be explained, and the relevance of sulphate adsorption to mineral weathering rates along altitudinal transects considered.

CHEMICAL TIME BOMBS IN EUROPE

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The environment in industrialized countries has long been the recipient of large doses of chemical inputs from numerous sources. In the face of perceived threats posed by these chemicals, policies have been enacted for protecting the public and the natural environment. The popular perception of societal risks from chemical uses, as reflected in current policies, appears to be biased toward the consideration of impacts relevant over relatively short time horizons. For example, while there are numerous concerns about reducing risks of explosions of chemical or nuclear plants, spills from oil tankers, and excessive use of potentially carcinogenic chemicals, the whole dimension of long-term environmental consequences of chemical uses has been largely ignored by the public and policymakers alike. Such lack of foresight is problematic because what appears to be ecologically sustainable over the short term may be clearly nonsustainable over the long term.

What is needed is a new paradigm for understanding the long-term accumulations of chemicals in the environment. As a first step, the factors influencing the storage and retention of chemicals need to be systematically analyzed. For example, for heavy metals the most important factors are: pH, redox potential, salinity, cation exchange capacity, and erosion potential. The next step requires information on chemical inputs; i.e., where the chemicals are accumulating in Europe. For heavy metals, the vulnerable areas are those with low capacities for retaining the chemicals and simultaneously receiving high chemical inputs. (The capacities are largely determined by the factors listed above.)

Moreover, it is important to note that the influencing factors can change in the future. Acidity of soils is of course influenced by acid deposition. Redox potential can change owing to drying out of wetlands, or flooding of dry lands. Salinity can change because of irrigation practices, saltwater intrusion of groundwaters, or sea level rise. Erosion can increase because of land use changes.

Thus, the capacities of soils and sediments determine the retention and release of numerous chemicals in the natural environment and specify the time scales over which deleterious ecological effects may occur. Hence strategies for preventing the long-term release of such materials must consider these capacities, and how they may shrink or expand in the future.

MODELING THE EFFECT OF VARIABLE GROUND WATER COMPOSITION ON SORPTION OF MOLYBDATE

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Laboratory batch and column experiments were used to identify mechanisms that could affect transport of molybdate in a large-scale natural-gradient tracer test. The tracer test was conducted at a site on Cape Cod, Massachusetts, to examine the transport and dispersion of solutes in a sand and gravel aquifer. A nonreactive tracer, bromide, and the reactive tracer molybdate, were injected as a pulse in July 1985 and were monitored as they moved as far as 280 meters downgradient through an array of multilevel samplers. The average rate of movement of molybdate was retarded by about 50 percent relative to bromide movement because of sorption onto the sediments.

Vertical gradients in ground water composition resulted in spatial variability in the mass of molybdate sorbed. These gradients were caused by mixing of a plume of sewage-contaminated water in the lower part of the aquifer with a zone of uncontaminated water that overlies the plume. The uncontaminated water has a specific conductance of 40 to 80 microsiemens per centimeter, a pH of 5.8, no phosphate, and 0.09 millimole per liter sulfate. Water in the plume has a specific conductance as high as 350 microsiemens per centimeter, a pH of as high as 6.7, 0.02 millimole per liter phosphate, and 0.45 millimole per liter sulfate. The transition zone between uncontaminated and contaminated water at the site is about 3 meters thick. During the tracer test, solutes traveled partly in the uncontaminated zone above the plume and partly in the underlying plume.

Sediment and water collected from the aquifer were used in the laboratory experiments to quantify the effects of variable ground-water composition on molybdate sorption. Sequential chemical extractions and x-ray diffraction data indicated that ferrihydrite coatings on sediment grains were the dominant sorbent. Phosphate and sulfate competed with molybdate for sorption sites in the laboratory experiments. Sorption of molybdate decreased as pH, sulfate, and phosphate increased; sorption increased as ferrihydrite content of sediment increased. Laboratory data were quantitatively modeled with the diffuse-layer model in the geochemical equilibrium speciation computer code MINTEQA2. Sorption is treated by the diffuse-layer model as a complexation reaction between a surface site and a solute, defined by an equilibrium constant. Nine surface-complexation reactions were required to simulate molybdate sorption in these laboratory experiments; two for hydrogen ion, three for phosphate, two for sulfate and two for molybdate. Equilibrium constants for sorption of hydrogen ion and phosphate were obtained from published sorption literature; equilibrium constants for molybdate and sulfate were fit to experimental data. One set of diffuse-layer model constants was used to simulate the experimental sorption data for the entire range of geochemical conditions considered.

The laboratory experiments predicted that horizontal molybdate velocities should increase with depth because of less sorption in the sewage-contaminated plume. These results agree with observations from the tracer test, where transport of molybdate in the upper uncontaminated zone lagged behind molybdate in the sewage-plume zone.

STONE LINES AND LATERITE FORMATION IN THE SOILS OF BAS-ZAIRE

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Some years ago the Prodaf (Projet de Developpement Agricole et Forestier) project was established in Bas-Zaire by Communaute Evangelique du Zaire (CEZ) in cooperation with SMF (Missionsförbundet). An investigation, supported by SIDA, was initiated last autumn on the situation of soils and erosion in that region (western Zaire).

In west central Africa tropical weathering has proceeded probably intermittently from late Mesozoic time. Very thick layers of ferralsalic soils have been formed on a weathered bedrock, consisting of Late Proterozoic rocks, mainly shales and sandstones.

During an early phase of the Panafrican orogeny the rocks were strongly folded and are richly penetrated by quartz in joints and dikes. Lateritic concretions occur in the soils and have been proposed to be of importance for the formation of regional platforms in the landscape.

Erosion has shaped a broken relief of deep valleys with steep sides, where gallery forests are remaining. Precipitation, restricted to eight months, is about 1200 mm/y. The recent erosion is intense and every brooklet is bearing sediment throughout the year.

Quartz fragments, liberated by weathering, are gathered in the basal zone of the soil and are the main constituents of a basal gravel, which also contains fragments of rocks and lateritic concretions. In the description of tropical soils such layers of gravel have been called stone lines. In Zaire the thickness of the basal gravel is considerable, changing between one and ten meters.

Different theories have been tried to explain this enrichment of remanent material in stone lines. Past climatic changes, resedimentation, soil creep or termite action have been proposed.

A possible connection between the formation of laterite concretions in the soil and the basal enrichment of quartz and laterite fragments is indicated by the present investigation. There are probably two effects, which both favour the enrichment of remanent material in the basal gravel:
1/ extraction and transport of iron, aluminium and silica by groundwater, 2/ termite action, with a biogenic transport to the surface of fine fractions in the soil.

Similar conditions with a basal gravel below weathered ferralitic soils seem to prevail in different parts of western and west central Africa. This basal gravel is of great importance for draining the soils and the ground water transport.

Calculating field weathering rates with PROFILE

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Abstract

A steady state soil chemistry model was used to calculate the base cation release rate due to chemical weathering rate for forest soils and surface water catchments. The model, PROFILE, is based on kinetic rate limited soil reactions and mass balance calculations for the different soil layers. From independently measurable soil properties, such as soil mineralogy, mineral texture, soil hydrology and deposition, PROFILE reproduces the observed soil chemistry, runoff water composition and chemical weathering rate at different 12 field sites throughout Europe and North America, reflecting large differences in mineralogy, texture, temperature and vegetation. The test show that the base cation release rate due to chemical weathering can be calculated with an absolute accuracy of ± 0.07 keq/ha yr in the range of rates from 0-5 keq/ha yr for both soils dominated by primary minerals and soils dominated by secondary minerals. A weathering rate map for Sweden for different cation release rates has been constructed using the model. Similiar maps have so far been made for Denmark and Maryland.

Mapping critical loads, weathering rates and geochemistry

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Abstract

In Sweden, critical loads for acid deposition to forests and groundwaters have been mapped using a mechanistic geochemistry model called PROFILE. The critical load for acid deposition depend much on the weathering rate in the system, as well as vegetation uptake of base cations and hydrology. The calculation model uses geochemical properties of soils as such as soil mineralogy, texture and temperature as input parameters to calculate the critical load. This study show how the critical loads and maps of critical loads and weathering rates depend on the weathering rate and further the parameters determining the weathering rate such as the mineralogy and texture of Swedish forest soils. The key minerals for determining the weathering rate have been identified as plagioclase feldspars, hornblende and epidote, all which occur in most Swedish soils. It can be shown that high critical loads and accordingly a high tolerance to acidic deposition coincide with locations with a certain type of mineralogy, texture or both.

DEVELOPMENT AND APPLICATIONS OF A MODEL FOR NH_3 VOLATILIZATION FOLLOWING SLURRY APPLICATION

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A mathematical model was developed describing gaseous NH_3 losses during the first days after application of nitrogen containing fertilizers.
Simulation modelling served two aims, the first one being the acquisition of a thorough understanding of the NH_3 volatilization process and its interacting subprocesses, the second one being the development of a decision supporting tool.
The model is both deterministic and mechanistic. It describes volatilization as a diffusive transfer of NH_3. In the case of spreading liquid manure, two stages are distinguished. In a first stage slurry is covering the soil, allowing the NH_3 in the manure layer to diffuse through the slurry-air interface, into the air. In a second stage, after complete infiltration of the slurry, NH_3 in the air-filled soil pores escapes through an imaginary boundary between soil pores and the outside air. The NH_3 concentration in the slurry and subsequently in the soil gas phase determines the magnitude of the volatilization flux. The NH_3 concentration in turn, is mainly influenced by the NH_4^+ concentration and the pH.
To calculate the NH_4^+ concentration, adsorption/desorption, nitrification, mineralization of the easily decomposable manure fraction and the NH_4^+/NH_3 equilibrium are considered. Furthermore, NH_4^+ can move through the profile both by diffusion and convection.
Describing the pH in a detailed way is complicated but necessary as pH is often found to be the critical factor for NH_3 volatilization. An attempt was made to model the fast pH changes in the upper few centimeters of a soil following slurry application and during NH_3 volatilization. The simulation results were compared with both field and laboratory measurements. In a final stage the model was used to calculate volatilization losses under different management practices such as ploughing the field either 2, 6, 12, 24 or 48 hours after manure spreading ; application of manure followed by irrigation ; and manure spreading on moist versus dry soils, windy versus calm days, warm versus cool days.
In this paper a comprehensive overview will be given of the different processes modelled, followed by a preliminary outline of the validation results and applications.

IS THERE ANY DIRECT PERCOLATION THROUGH "BY-PASS" CAUSING GROUNDWATER POLLUTION TO DEEPER AQUIFERS ?

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It is becoming remarkable that confined groundwater has been gradually polluted by chemical substances such as Trichloroethylene and Nitrate, but behavior of pollutants in deep aquifers has not been explained. Many researchers in the world have detected chemical substances originated from human activities such as agriculture and livestock farming in deep confined groundwater. Transit time of groundwater from land surface to more than 100 m deep is theoretically considered to be over 50 years from hydrogeological point of view.

The author collected water from each aquifer of the multi-screened well and analyzed water chemistry for it. Quality and temperature of groundwater for each aquifer were quite similar with each other. He also tried an experiment on continuous withdrawal from the 170 m-deep-well setting screens below 120 m deep only. Another 160 m-deep-well setting seven screens from 39.5 m to 154.5 m below the land surface exists near the experimental well. The distance between the two wells is about 50 m. With passing the time, Nitrate concentration in groundwater from each aquifer of the experimental well significantly increased. They are good evidences of existence of some direct percolation route, so called "by-pass", where upper groundwater goes quickly down to lower one. It is considered that these "by-passes" play very important role for deep groundwater pollution.

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HEAVY METALS AT A SHOOTING RANGE; ENVIRONMENTAL RISK AND POTENTIAL METAL RESOURCE.

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Introduction

The present study deals with the negative impact of increased heavy metal abundances in soil in the vicinity of shooting ranges, Viikinmäki, Helsinki. The estimated annual load of heavy metals (lead, copper and zinc) in the area is 15,000-18,000 kg including lead pellets,bullets and their splinters.

Sampling and analytical methods

The accumulation of lead pellets in the soil of the outfall area of the shotgun ranges was determined by taking soil samples with constant surface area. The bullet metal contents in range butts were determined by taking soil samples with an accurately known volume from representative sites in the embankments.

To establish the degree of pollution, soil profiles were studied. The samples were analysed for As, Cu, Ni, Pb and Zn by the ICP-AES method. The contamination of groundwater and surface water was also investigated. The samples were analysed for As, Cu, Ni, Pb, and Sb by AAS graphite furnace method and Zn by flameless AAS.

The possible migration of pellet lead from the soil to plants was studied in three plant samples. Composite samples of mushrooms *(Cantharellus cibarius)* and stems and berries of lingonberry *(Vaccinium vitis-ideae)* were collected from the outfall area of shotgun ranges. The samples were analysed for As, Pb and Sb by ICP-AES.

The minerals formed in the course of pellet weathering were studied under the microscope and with the X-ray diffraction technique. Different weathering products and their mineral compositions were established with a Debye-Scherrer camera.

Results

At the shooting range, at least 176 000 kg of pellets occur in an area totalling 4,37 ha. The lowest limit of concentration used is 1 kg/m^2. The maximum concentrations were above 20 kg/m^2. The butts contain at least 46 000 kg of bullets and their splinters.

The soil is strongly contaminated indicating rapid transformation from the metal phase into weathering products.The lead content of the dissolved and reprecipitated lead in the soil varied from 122 ppm to 4%. Lead content in the groundwater was 405 μg/litre. The maximum heavy metal concentrations in plants were found in mushrooms, the lead content being 498 ppm.

Mineralogical studies showed that the weathering crust of pellets is composited of anglesite crystals and a mixture of cerussite and hydrocerussite.

Contaminated soil at shooting ranges can be at least partly rehabilitated.Dressing tests indicate that lead pellets and bullet remnats can be separated from the soil matrix by using simple dressing technology.

THE USE OF LAKE SEDIMENTS IN MONITORING HEAVY METAL POLLUTION

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Between 1873 and 1984 the Geological Survey of Finland carried out geochemical mapping based on lake sediments. About 16 000 organic-rich sediment samples were collected from an area 80 000 km^2 at an average sampling density of 1 sample/ 5 km^2. Samples (volume 0.2-0.5 litres) were taken from the upper part of the sediment layer. The samples were dried at 70-80 C° and ignited at 500 C°. Ashed samples were analysed by AAS and drawn to maps at the scale 1:100 000. Sediment samples were stored for later use.

The aim of the present study is to examine the possibility to use the old lake sediment samples in monitoring for heavy metal pollution. For this purpose 144 new lake samples were collected in 1990 from five different test areas representing time interval 8-15 years. Samples were taken as close as possible to the previous sampling sites and were dried and ignited analoguously with older samples. New and old samples were analysed by Plasma Spectrometer (ICP-AES) after aqua regia leach for 31 elements.

Sample error was tested by 28 dublicate samples. The relative error for each element was determined. The preliminary results show that the relative error is quite low beeing f.ex. for Zn, Cu and P under 35 % throughout the whole concentration level. Correlation calculations (Spearman's rank correlation coefficient) gave very high positive correlations between the contents in original and dublicate samples (f.ex. P: 0.9885, S: 0.9606, Zn: 0.9539, Cu: 0.9695, Pb: 0.8835).

One test area comprises the surroundings of Siilinjärvi town which is situated 20 km north from Kuopio. In this area some lakes show a clear increase of heavy metal and nutrient concentrations. For instance in 97 % of cases S contents have increased during 10 years. The average increase is 200-300 %, but in one lake the increase of S content is fifteenfold. The most eastern test area is situated very close to the Russian border representing uninhabited region. In this area no systematic increase in heavy metal contents exists.

ENVIRONMENTAL GEOCHEMISTRY AND HEALTH IN THE 1990s
A GLOBAL PERSPECTIVE

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The foundations of geochemistry and health are associated with work in Canada, USA, USSR and UK in the 1960s and parallel studies in geomedicine in Scandinavia. The development of geochemical mapping techniques and compilation of geochemical atlases have led to innovative multidisciplinary research into their applications in the areas of agriculture and land use, fresh water quality for irrigation and potable supplies, estuarine and coastal waters and fisheries, medicine and public health, and environmental pollution. Recent developments have concerned the influence of geochemistry in wildlife nutrition. Research in urban geochemistry has been applied to the modification of the chemical environment in towns and cities arising from urban and industrial development.

Communication and international collaboration within the discipline has been encouraged through 25 Annual Conferences on Trace Substances in Environmental Health at the University of Missouri, Columbia, USA and several symposia in London and Oslo and promoted by the Society for Environmental Geochemistry and Health and the Society's journal 'Environmental Geochemistry and Health'. The International Working Group on Geochemistry and Health and Disease was established by IAGC.

Throughout the 1970s and 1980s the main centres of research have been in China, Scandinavia and the UK, with smaller though significant programmes in many other parts of the world. As geochemical maps and atlases continue to cover greater areas, the 1990s will provide an exciting opportunity to study the global significance of many of the problems previously studied on a local or regional scale.

Areas of particular interest include: (a) the impacts of metalliferous mining and smelting on soil and water quality; (b) the influence of mineral deficiencies and excesses on the nutrition of farmed livestock and wildlife and on the ecosystem; (c) the influence of geochemistry on human disease, including selenium responsive diseases and endemic fluorosis and goitre; (d) the modification of the natural geochemical environment by urban and industrial development.

HYDRATION, SWELLING AND STRUCTURE OF DIFFERENT CLAY MATERIALS

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A B S T R A C T :

Eight clay materials : hectorite, Wyoming montmorillonite, Camp Berteaux montmorillonite, Allentown nontronite, Santa-Ollala vermiculite, Esperce clay, Vosges illite and Georgia kaolinite were saturated by five cations : Mg, Ca, Li, Na and K, weight and volume gains were followed until the saturation points were reached. The experiments were performed in pure water at 25°C, in pure water at 80°C, and in saline water (I = 2) also at 25°C. The parameters influencing the swelling are the layer charge, the nature of exchangeable cations and the water activity.

The structure of water saturated clay systems has been determined by the use of electron microscopy.

MECHANISMS FOR RECYCLING OF SULFUR IN LAKE SEDIMENTS

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In many lakes only a small fraction of the sulfide produced from dissimilatory sulfate reduction becomes bound in the sediments as iron sulfides or organic sulfur compounds. The majority of the sulfide is rapidly reoxidized, and each sulfur molecule is cycled many times between oxidized and reduced forms. Porewater profiles may be used to calculate the net flux of sulfur into the sediments, but at each depth concentrations represent a steady-state between rates of oxidation and reduction. The rates and mechanisms of this recycling are poorly understood. The objectives of this study were to measure the rates of sulfate reduction and sulfide oxidation in the sediments of a eutrophic hardwater lake, and to determine the probable electron acceptors involved in the sulfide oxidation. Rates of sulfate reduction were measured with $^{35}SO_4^{2-}$ in intact sediment cores. The net rate of sulfur storage in the sediments was measured in dated sediment cores and calculated from a lakewide mass balance. In addition, numerous measurements were made with benthic flux chambers of fluxes of sulfate, oxygen, nitrate, iron and manganese across the sediment-water interface. Together with profiles of dissolved species in porewater, these measurements allow the calculation of sulfur fluxes and electron transfers within the sediments. As observed in numerous other lakes, rates of sulfate reduction in Lake Sempach (900-13,000 mmol $m^{-2}yr^{-1}$) are high and comparable to rates in coastal marine sediments. The rate of sulfur storage in the sediments is less than 5% of the rate of sulfate reduction. Approximately 50% of the sulfide is reoxidized by the mat of Beggiotoa that overlies the sediments. Most of the remaining sulfide is oxidized in permanently anoxic sediments. Porewater profiles indicate that reductive dissolution of both Fe and Mn oxides occurs in the zone of sulfide reduction. The porewater profiles and profiles of Fe and Mn in the solid phase of sediment cores suggest that Fe oxides are relatively more important as electron acceptors in this lake.

HEAVY METAL FRACTIONATION IN NATURAL AND POLLUTED STREAM SEDIMENTS, TORDERA RIVER BASIN, CATALONIA, NE SPAIN.

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Previous stream sediment geochemical studies in the Montseny area (Barcelona and Girona provinces, Catalonia, NE Spain) have shown anomalous areas of both natural and anthropogenic origin. Sulphide mineralizations with galena, sphalerite, pyrite and chalcopyrite are known and detrital grains have been recognized in natural metal-rich samples. Pollution comes from industrial and urban sources. The environment is siliceous and surface waters are nearly neutral.

An attempt has been made in order to characterize the fractionation of Pb, Cu, Co, Ni, Cd, Cr, As, Se, Sb, Bi and Hg in natural and polluted samples. Iron and manganese have also been analyzed. Several total non-selective extractions and selective sequential schemes have been tried. All elements have been determined by flame, graphite furnace, hydride and cold vapour AAS.

For total, non-selective extractions three acid attacks give the best results : aqua regia, nitric-hydrochloric and hydrochloric-nitric-hydrochloric. The extracted metal varies according to the element and the reaction site. For most metals aqua regia is the least effective. High concentrations of Pb and K in some samples preclude the use of sulphuric and perchloric acids.

Among the methods of sequential multiple extractions tried, the following gives consistent figures and is easily compatible with the determination method (AAS) with the sole exception of mercury with the ammonium acetate extraction. The used scheme is :

1- Water soluble, exchangeable and some carbonates: ammonium acetate.
2- Manganese oxides : hydroxylamine hydrochloride

3- Organic matter and some sulphides : hydrogen peroxide.
4- Amorphous iron oxides : Tamm's reagent in the dark.
5- Crystalline iron oxides : Tamm's reagent under UV light.
6- Residual minerals and metal compounds : aqua regia.

No disolution of residual crystalline fraction with HF and other acids is made because previous works show a very small and no significative metal content in the aqua regia residue.

Results reveal a sharp fractionation difference between natural and polluted samples. Taking the highest value of the total acid extractions as the total metal available, fraction 1 is the most important and have 20 - 55% of the total metal in polluted samples whereas for naturally enriched samples fraction 6 is usually the most significant and often have less than 20% of the total metal in fraction 1. Moreover, amorphous iron oxides are richer than crystalline for polluted samples and the opposite is found in the non-polluted. All the studied elements show known behaviours in their fractionations in organic matter, iron and manganese oxides.

PROSPECTS ON THE USE OF SPECIAL COMPUTERIZED SYSTEMS TO CONTROL THE CONTAMINATION OF SOILS AND WATER SOURCES IN RUSSIA

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At present, taking into consideration that the most degraded ecosystems are agrosystems occupying about 60% of all the territories, their control is an urgent and complicated problem. The use of chemicals and other technologies, not always justified environmentally, leads to a decease in natural resistance of agroecosystems to outer impacts. This situation is aggravated because industrial plants are amassed on such territories, and they are capable of emissing toxic substances into the atmosphere and increasing an environmental load on soils and water sources. An additional difficulty to organize environmental control services is that local agroecosystems (ecosystems) on the Russian territory are placed in conditions quite different with climatic characteristics and therefore are subject to most various loads owing to differences in a reaction to agricultural technologies as well as to industrial emissions and their nature.

So when organizing environmental monitoring services in Russia it is necessary not only to approach a solution of this task on the basis of control principles used in studying large complex systems but, taking into account a necessity to carry out such control on a great number of factors, to do it practically continuously in time and space. A similar task can be decided only by the use of special computerized environmental control systems.

Since I989, headed by the All-Union Research Institute of Fertilizers and Agropedology, the USSR has begun to develop a multi-level computerized environmental control system with a high degree of versatility and capable of providing for an operative control of more than 64 main parameters (physical, chemical and biological) of air, soils and waters. With small modifications, individual blocks of this system may be used to control the contamination of sea waters.

ENVIRONMENTAL GEOCHEMICAL MAPPING BASED ON SMALL HEADWATER STREAMS IN FINLAND, PRELIMINARY RESULTS

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A very sensitive element in the environment to react anthropogenic factors are surface waters in streams; the organic streamsediment is known to be a very effective collector for many heavy metals. An environmental geochemical mapping program to separate the anthropogenic effect from geological features was therefore decided to carry out in Finland by using stream water samples together with organic stream sediments.

The total amount of 1183 small drainage areas (30 km^2 in an average) were sampled during a five week period in August-September 1990 covering the whole Finland by the Geological Survey. The sediment samples were composites of 3-5 subsamples collected from separate streams inside the chosen drainage area. The samples were wetsieved to get loose and fine material as humusrich as possible. Water samples were single samples from the outlets of the drainage areas. Sampling density was 1 sampled drainage area per 300 km^2.

In the laboratories of the Geological Survey the sediments were dried (60°C) and homogenized. After extracting by hot 7.25 M HNO_3, the consentrations of 30 elements were determined by ICP method. Later on the easily leachable (bioavailable) fractions will be analyzed.

The water samples were analyzed for pH, colour, electrical conductivity and alkalinity values and later on they will be analyzed for five more anions and 16 cations.

The same samples will be analyzed for chlorophenols and some other chlorinated carbon compounds and microbiological properties by the National Public Health Institute.

As examples of the results pH values, electrical conductivity and alkalinity of stream water as well as heavy metal and chlorophenol concentrations of sediments are presented. These preliminary results show that geological factors like the type of bedrock, abundance of peatlands and marine sulphide-bearing clays in the overburden have the strongest influence on the quality and element consentrations of water and sediments, but also some anthropogenic efects are clearly visible. The buffering capacity of the stream water proved to be as its lowest in the granitoid areas.

INVESTIGATION OF METAL CONTENTS IN LAKE SEDIMENTS WITHIN THE COUNTY OF UPPSALA.

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ABSTRACT

Natural processes and human activities mobilize and redistribute naturally occurring elements which in excess concentrations and in the wrong place become pollutants or toxic to biological life. For instance, industrialized countries have increased metal contents in the air, soil and water systems. Therefore it is very important to monitor ecosystems and their pollutant contents once in a while.

In order to investigate and quantify the natural occurrence of elements (specially heavy metals) in the numerous small lakes within the county, a project was initiated by the Environmental Protection Office (Miljökontoret) in Uppsala. The project started in August 1989 and the ambition has been to investigate twelve lakes per year. The results presented here are for the first twelve lakes studied.

The investigated lakes are not subjected to the impact of sewage-effluents. The sources of pollutants, if any, to the lacustric water and sediment are wet and dry depsitions from the atmosphere and the drainage systems of the recharge area.

Sediment samples are taken from the deepest parts of the lakes where vertical mixing is minimal. The sediment-cores were about 25 cm long. The top 1 cm, 11-12 cm and 22-22 cm layers of the sediment-cores were analysed. The top layer represents recent years while the 22-23 cm layer represents the pre-industrial period. The metals analysed included the more toxic elements Cd, Hg, Pb, Cu, Zn, Ni, Co, As; the toxic but mor rare elements W, Zr, Nb, Ba, Ti and also Na, K, Mg, Ca, Cl, Cr, V, Rb, Sr, Al, Br, Az, Mo, Si, P, O, Mn, U, S, Fe, Ba.

The results of the analysis show that most of the metals are present in low concentrations. Certain mtals such as Cu, Zn, and Ni show concentrations hiher than backgroun-values. In most of the lakes the mercury concentrations are below detection limit. Results from some forest lakes in the eastern part of the investigated area show higher values. Owing to the dominant wind directions of the region, these values may be indications of windborne deposition from the combustion of the energy supply station in Uppsala.

ANTHROPOGENIC EMISSIONS OF SELENIUM IN FINLAND

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The biogeochemical cycling of selenium through the environment is currently disturbed by anthropogenic activities such as the mining and refining of ores and fossil fuel combustion. Approximately 13000-19000 ton selenium is cycled through the troposphere annually,30-50 % is anthropogenic in origin.

Finland is a country with a low selenium concentration in the environment because of geological reasons. It has been suggested that the low selenium intake is associated with the cardiovascular disease incidence. To increase the domestic food selenium level, selenate has been added nationwide to fertilizers in Finland. However, other anthropogenic selenium sources in Finland have not been studied. The aim of this study was to estimate the proportion of the anthropogenic emission of selenium to the atmosphere, fallout of selenium from precipitation, and to compare it with the selenium used in fertilizers.

Samples of main primary energy sources and rain and snow were collected and analysed for selenium. Emission factors for some energy sources and nonferrous metal production were adopted from the literature.

The total annual anthropogenic emission of selenium to the atmosphere in Finland was about 27.3 ton in 1989, 65 % from nonferrous metal production (copper 10.34 ton,selenium 3.92 ton, zinc 3.26 ton, nickel 0.27 ton), and 35 % from primary energy consumption (oil 5.40 ton, coal 2.78 ton, peat 1.25 ton,fuelwood 0.052 ton).The selenium fallout from precipitation was about 15.7 ton, of which 81 % from rain and 19 % from snow, based on a mean annual rainfall of 600 mm and a selenium concentration of 125 ng/l in rain and 30 ng/l in snow. About 75 % of the selenium in snow was selenite. The amount of selenium used in fertilizers was 11 ton in 1989.

In conclusion, the anthropogenic emission of selenium to the atmosphere in Finland was roughly 0.46 % of the global emission, copper smelting accounting for 38 %. Oil was the main source of the selenium emission from primary energy consumption. The amount of selenium fallout from precipitation was 58 % of the total estimated anthropogenic emission and 40 % higher than the amount of selenium added as fertilizers. More research is needed for the study of airborne selenium as a source of environmental selenium.

GEOLOGICAL CHARACTERISTICS OF A GREENHOUSE GAS--METHANE

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Man is slowly but significantly attering the global environment of the earth. Methane, an important greenhouse gas, is the most abundant organic gas in the atmosphere. Its rapid increasing in the earth's atmosphere make it necessary and urgent to research its relationship with various natural courses and human activities. In this paper, geochemical characteristics of methane and other hydrocarbon gases in soils of different geographical and geological environments will be discussed.

Methane and other hydrocarbon gases exist in soils in various forms, but mainly are three: the free, the absorbed and the dissolved. Among them, the absorbed is the most predominant. Exhaustion of methane from soil to the atmosphere is controlled by many chemical and physical factors. Methane concentration in soil is one of them.

There exists large difference of hydrocarbon concentration in different type of soils in China: In the arid northern China, methane concentration in soil of loess area is about 213 μl/kg, heavy hydrocarbon gas (C_2-C_5) is about 19.5 μl/gk, in desert area methane concentration in soil is about 49.5 μl/kg and heavy hydrocarbon 4.6 μl/kg; In the humid southern China, methane concentration in Hainan Island is about 14.5 μl/kg, heavy hydrocarbon is 3.4 μl/kg, in oil field area of Guangxi, soil methane concentration is about 53.6 μl/kg, and heavy hydrocarbon 18.1 μl/kg.

Concentration of hydrocarbons in soil is related to source of hydrocarbon and soil property. Soil methane concentration in loess area is higher than that in desert area, because loess has good preservation to hydrocarbons. In the south of China, climate condition make it easy for plant to grow, organic matter in soil is abundant, and bacteria activity is prevailing in soil, so it could be conceived that there is good source of methane in soil of this area. But because of its strong soil acidity and prevailing water penetration, preservation of hydrocarbons in this type of soil is poor, for it is difficult to form secondary carbonate, a main hydrocarbon absorbent. Therefore, relative to the northern part of China, concentration of methane in soil of this area is lower and contribution of methane to the atmosphere is larger. In oil field area, because of very good hydrocarbon source, soil methane concentration is higher, and contribution of methane to the atmosphere is also often larger than that of other area.

GEOCHEMICAL FACTORS CONSTRAINING THE EFFECTIVENESS OF STORM-WATER CATCHMENT RESERVOIRS IN ALLEVIATING METALS POLLUTION OF FALSE BAY, CAPE PROVINCE, SOUTH AFRICA

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A geochemical study of sediments in Princess Vlei, south-east of Cape Town, has implications for the effectiveness of storm-water catchment reservoirs in retaining anthropogenic metals along the coast of False Bay, and in other similar areas underlain by sands.

False Bay, the largest bay on the southern African coast, is bounded to the north by the Cape Flats, a low area of Pleistocene to Recent aeolian sediments, largely quartz sands of high purity. The bay faces a severe threat of pollution as a result of human settlement of the Cape Flats. Prototypical detention ponds have been introduced to curb the flow of storm-water into the bay. Until now, the major concern has been bacterial pollution, owing to a prevalence of informal habitation. However, future increased supply of metals to the bay can be expected with the establishment of new urban areas and the growth of industrial activities.

An investigation of potential residence sites for polluting metals, was undertaken in the sediments of Princess Vlei, one of a number of shallow lakes, or "vleis" on the Cape Flats. The 35 ha, 2 m deep lake receives stormwater run-off from a residential area and a small industrial estate; water flows out to another vlei and eventually to False Bay. Princess Vlei was chosen for the study because its acutely disturbed ecosystem, almost complete absence of macrofauna in the sediments, and intermittent declines of the fish population, have been attributed to past heavy metal pollution, specifically by chromium.

Extensive hand coring and a small vibro-corer were employed to map the sediments of the lake floor. Optical microscopy and XRD have confirmed the simple mineralogical character of the sediments with quartz being the only major mineral present. Nevertheless, Cr concentrations of 120 ppm, significantly above background values, were recorded during XRF analysis of bulk sand samples. In the almost complete absence of clays, with which Cr and other heavy metals most readily bond, potential residence sites appear to be limited to (i) fine organic matter (ii) ferric oxide/hydroxide coatings on sand grains, and (iii) ferricrete nodules and layers. Provisional analyses suggest that the ferricrete and oxide/hydroxide grain coatings are significant sites of Cr accumulation. Results of leaching experiments on these inorganic, as well as the organic sediment fractions, will be presented.

Despite the generally acidic nature of the soils surrounding Princess Vlei, the lake water is alkaline at most times. The extremely small carbonate content in the lake sediments, however, results in a low pH buffering capacity . As a consequence, an influx of water of differing pH during storms, or perturbations within the lake, might significantly affect pore-water pH. Local changes to a more acid condition might adversely affect the ability of the sediments to retain metals.

Physical evidence to demonstrate the transfer of soil lead into young children via hand to mouth activity.

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Numerous exposure modelling studies have emphasised the importance of involuntary ingestion of dust and soil as an extra route of exposure of young children to lead in addition to diet and water, the main routes in the adult. Previous studies have shown that lead can be measured on childrens hands and that statistically significant relationships exist between floor dust lead loading, handwipe lead and blood lead. Furthermore at least some of the lead on the hand has been shown to be particulate.

Automated scanning electron microscopy has been extremely valuable in the consideration of the sources from which housedust lead originates. The importance of paint as a dominant source in UK homes, particularly those with extremely high concentrations of dust lead, has long been recognised. More recently, however, an improved assessment of the contribution of soil and external dusts has shown that they too make a considerable contribution. In other countries, including large parts of the USA, children spend a much higher proportion of their time outdoors and so this contribution may be even more important. The USEPA has targetted this exposure in recent times and focussed research into the establishment of guideline concentrations at which exposure may be considered to be unduly harmful.

In order to extend the automated SEM technique to quantify the contribution of lead particles from different sources to particulate matter on childrens hands, and to allow comparison with existing data on housedust, a new handwipe method was developed. This has been applied in a study in Winster, Derbyshire, UK, a well known "geochemical hotspot" where natural mineralisation and extensive mining of lead have resulted in high concentrations of the metal in soil and dust. The methods used and the results from this case study will be discussed.

SUBMICROMORPHOLOGICAL PROPERTIES OF SOME MINERAL NEOFORMATIONS DERIVED IN THE SOIL ENVIRONMENT AS A RESULT OF COPPER SMELTER ACTIVITY

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Micromorphological and submicroscopic properties of some industry originated sediments derived close to dump have been investigated. The dump consist of glossy and fine crystaline material left after melting, which was stored near Głogów copper smelter, Lower Silesia, Poland. Material of dump was leached with rainfall water, consequently easy soluble substances were washed out and deposited at local depressions. It has been found that sediment under study consist of two layers and characterize itself by clay and sand texture, respectively. Both materials indicate pH 7.0 and 7.2 and show very same chemical composition. They consist mainly of calcium (about 13%) and sulphur (about 9%) and contain respectively high levels of copper and lead (till 1100 mg/kg). X-ray diffraction analysis pointed out that sediments of both layers consist mainly of gypsum.

Micromorphological examination of thin sections from surface layer indicated that this material consist of colloidal substances impregnated with microcrystalline calcite and larger gypsum crystals occurring as rosette concentrations in some places. Secondary calcite cutans associated with planar voids have been found in some places as well. Deeper layer consist of sand size spherulitic concretions of gypsum. Electron image analyses pointed out the presence of two different kinds of spherulitic gypsum concretions. Forms with rosette or radial arrangement dominated, however compound mantle spherulites were found as well. The latter consist of oval non-crystalline calcareous center and external part build up of gypsum.

Investigations clearly indicate that near the copper smelters industry originated calcite and gypsum minerals could be formed. They are deposited as calcareous-sulfate colloidal sediments, as a result of washing out of smelter dump. At the first stage sulfate material is reorganized and fibrous minerals of gypsum are crystalized. They grows giving rosette forms and next spherulitic concretions. Calcareous components are washed away, and finally sediment is dominated by sharp boundary gypsum spherulitic concretions which are coated by calcite cutans.

SOIL MINERAL WEATHERING: EFFECT OF PORE SIZE DISTRIBUTION AND FLOW RATE ON MACROSCOPICALLY OBSERVED REACTION RATES

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INTRODUCTION

The estimation of realistic field rates of primary mineral weathering can be essential in assessing long term effects of acid rain impact on soils.

Rates obtained from laboratory studies are 2 to 3 orders of magnitude higher than field rates obtained from budget studies. Apparently some constraint that limits weathering in the field is released in laboratory studies.

Most laboratory methods for measuring weathering rates aim at optimizing 1) contact between solution and mineral surface and 2) solution transport of reactants.

METHODS

A simple 2D model (fig. 1) that simulates packing of spherical particles, is used to:

1) Estimate pore size distributions from particle size distributions (fig.2)
2) Calculate the relative contribution of pores to total water flux, using Poiseuille's law. ($Jout \approx R^2_{pore}$)
3) Calculate the distribution of reactive pore surface.
4) Calculate distribution of Péclet numbers (α).

   $\alpha = L*J_p/D_{mol}$ L = estimated pore length

   J_p = pore flow velocity

   D_{mol} = coefficient of molecular diffusion

   Péclet numbers smaller then 1 indicate diffusion dominated transport and larger then one convection dominated transport.

RESULTS

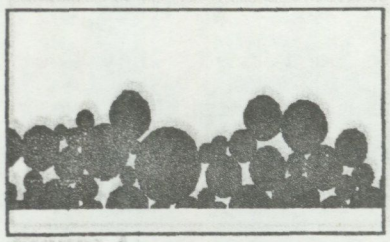


Figure 1: *Example of 2D particle packing model*

Fig. 2 shows particle size distribution and calculated pore size distribution of a silty soil.

Fig. 3 shows that a minor fraction of total pores gives a major contribution to the bulk water flux. At least 60% of "reactive" surface is located in pores that contribute only 10% to the bulk water flux.

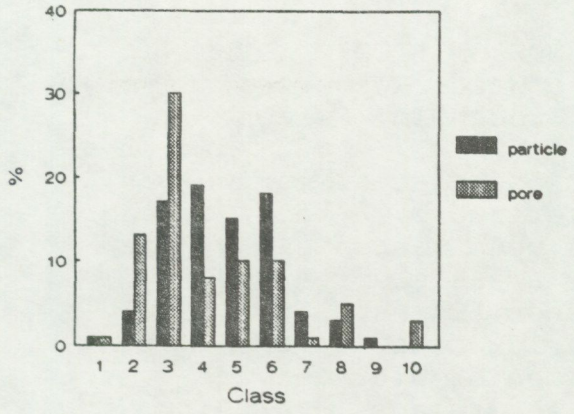


Figure 2: Distribution of particle radii (5-30um) and pore radi (2-15um)

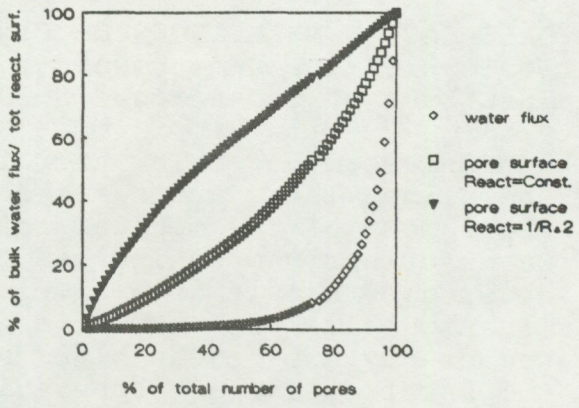


Figure 3: Relative contribution of pores to volume flux of water and pore surface

Calculation of Péclet numbers at different bulk flow rates show that at a bulk flow rate >20mm day, transport in all pores is dominated by convection. Laboratory column studies are usually carried out at flow rates > 20mm/day.
Reduction of the flow rate to 2mm/day bulk flow which is close to the field situation, gives diffusion controlled transport in 90% of the pores.

Initial calculations for feldspar minerals show that if the distance of diffusion in diffusion dominated pores exceeds 10-100*(particle diameter), *inter-particle* diffusion becomes slower than surface reaction rate.

The macroscopically observed chemistry of column output will then be affected by flow rate and pore size distribution. These factors are studied in laboratory experiments with soil columns.
Results of laboratory studies will be presented in the final paper.

CONCLUSIONS

Model calculations and experimental data show that *inter-particle* diffusion might limit transport of reactants from and to the mineral surface dependent on pore size distribution and flow rate. The discrepancy between field and laboratory weathering rates might be explained by the elimination of diffusion limitations in the latter.

BASE CATION NUTRITION FOR PINE STANDS ON LITHIC SOILS.

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In Fennoscandia, below the highest postglacial marine shoreline, large areas are characterized by a rocky ground, where most of the mineral soil has been washed off by the waves of the regressing sea. These areas are sparsely covered by slowly growing pine stands. The shallow, mostly organic soils are very acid and enriched in nitrogen, supposedly due to the high deposition of nitrogen and sulphur from the atmosphere in recent decades. It is therefore plausible that an unbalanced nutrition situation could arise by a disproportion of Ca, Mg, K and P in relation to N. The aim of this study has been to find out whether these pine trees receive their nutrients from the atmospheric input or from weathering of primary minerals in the bedrock.

The sources of base cations have been evaluated by using Sr isotopes as analogues for Ca. Sr in wet (and dry) deposition has an isotopic composition similar to that found in sea water and in carbonate rocks, while the Sr derived from the rock is enriched in ^{87}Sr coming from radioactive decay of ^{87}Rb. By treating the Sr found in pine wood as a binary mixture of Sr from deposition and Sr derived from the rock, it is possible to calculate the relative importance of these two sources.

In four out of five investigated sites the rock derived Sr (Ca) in pine wood was in the range of 25-35%. In the fifth site the percentage was 88%. The reason for these differences could be found in the bedrock composition. The former areas consisted of more acid gneisses and granites, while the latter area had a gneissic rock richer in easily weatherable minerals like biotite and hornblende.

Previous studies of runoff water from rock surfaces covered by shallow organic soils indicate a weathering rate in the order of 100 M of charge per ha and year. The growth of the pine stands has been estimated to about 0.25-0.60 m^3 per ha and year and the biomass accumulation of nutrients to about 10-20 M of charge per ha and year. Most of the base cations derived from weathering and atmospheric deposition is thus lost by runoff. The anions accompanying these base cations are mainly, in descending order, sulphate, organic anions and nitrate. Signs of an unbalanced nutritional situation can, in the studied sites, be observed as low ratios of Ca/N, K/N, Mg/N and P/N in needles and as yellowing of needle tips. As the growth of these stands is still limited by water deficiency, the unbalanced nutritional condition is likely to aggerate in years with abundant rainfall during the growing season.

THE CALCULATION OF BACKGROUND SULPHATE CONCENTRATIONS IN NATURAL SURFACE WATERS IN SWEDEN, AN ATTEMPT.

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In order to measure the extent of acidification are the background, "preindustrial" conditions important to establish.
An equation for the calculation of background concentrations of sulphate in surface water in Norway has been published by Henriksen. When applied on data from the Swedish lake survey in 1990, covering 4000 lakes, it was found that the calculated background concentrations exceeded those measured in about one third of the lakes. Therefore the way of calculation had to be revised.
The proposed revision is based on background concentrations in precipitation and estimated contributions from the soil. Three different ways are tried to establish the contribution from weathering; recalculation of present data, geological ratios as a basis, and historical data on denudification. It is however clear that local sources of sulphur as pyrite soils and sulphide minerals as well as sinks in form of peat land are impossible to handle in a more general equation.

ANTHROPOGENIC INPUT OF ZINC, LEAD, ARSENIC AND COPPER INTO SEDIMENTS IN A CUT-OFF RIVER BED NEAR CAPE TOWN

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A reconnaissance survey has been made of pollution resulting from surface runoff from an urban industrial area into sediments formed in an old cut-off river bed, which now comprises of a number of broad pans interconnected by narrow vegetation-filled channels which are dry in summer and flooded in winter (maximum depth ~1.5m). The river bed is situated in a narrow zone (100-200m wide) between a residential area and a light industrial area which borders on the sea. The aim of the research was to evaluate the effectiveness of the sediments and vegetation in the river bed in trapping and holding metal pollution in an area that is proposed as a recreational and conservational facility.

Twenty-two sediment cores were taken in both wet and dry conditions using PVC tubing. The sediment cores were divided into three or more sub-samples (68 in all) based on visible lithological boundaries in the sediment. Particle size analyses and qualitative XRD analyses were carried out on thirty representative samples. Thirty-one major and trace elements, including Cl, S, Mo, Pb, Br, Se, Bi, W, As, Zn, Cu and Ni, were determined by XRFS in all samples. Samples were analysed for C, H, N and CO_2.

Unusually high concentrations were found for Na_2O (0.2-21%), Cl (.01-11%), S (.04-1.7%), P_2O_5 (.07-1.4%), Br (1-320ppm), Zn (3-3700ppm), Pb (4-760ppm), As (1-32ppm) and Cu (2-125ppm). The Na, Cl, S and Br are probably derived from airborne sea spray and underground incursion of sea water and have been concentrated by repeated evaporation cycles. The source of the P is probably domestic and industrial detergents, while Zn is sourced from Zn-plated steel roofing materials and Pb from gasoline. Apart from the marine-sourced elements the input to the sediments is mainly by surface run-off via storm-water drains.

Except for a very thin (<2mm) oxidised surface layer the sediments are highly reduced with a high organic matter content, and pyrite was identified in a number of samples. The heavy metals are concentrated in the upper layers of the sediments. Statistical analyses indicate that Zn is associated mainly with the organic matter, while Mo and Pb are incorporated into the sediments as sulphides. Arsenic is associated with both organic matter and clay minerals and Cu with both organic matter and sulphides.

The sediments and vegetation in the river-bed act as a very efficient filtering mechanism, the heavy metals being trapped and held in the sediments very close to their entry-points (storm-water outlets).

DEGREE OF POLLUTION OF THE SEDIMENTS IN LAKE KETELMEER AND LAKE IJSSELMEER AS AFFECTED BY THE RIVER RHINE

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The sedimentation area of the northern branch of the river Rhine (river IJssel) is lake Ketelmeer. This fresh water lake, situated between two polders (reclaimed in 1940 and 1957) has an open connection with the largest Dutch lake IJsselmeer. Based on sampling of the topsediment and deeper a comparison between the two lakes on heavy metals, polychlorinated bifenyls and other pollutants could be made. The youngest geological layer in this area, the IJsselmeer-deposit (IJm-deposit), sedimented since 1932, shows variations in soil quality in place and time. The chemical analyses of the samples were corrected according to a Dutch standard system. The average quality of this deposit in lake Ketelmeer is, compared to Dutch standards, on an unacceptable level. The quality of the toplayer of this deposit can be stated as polluted (table 1). In lake IJsselmeer, this type of deposit is located in deep specific sedimentation areas only. The toplayer is merely slightly polluted. In the sandy areas the degree of contamination in the topsediment is on acceptable levels. In the toplayer of the IJm-deposit the clay- and organic matter content are the same in both lakes. During the last decades the carbonate-content in lake IJsselmeer increases due to an increase of the pH (algae blooms).

By sampling sandpits and deeper zones in both lakes, concentration-profiles for several polluting compounds during the last 60 years could be derived. These profiles show a similar shape in both lakes. The industrial production prior to the second world war in the period 1935-1940, the industrial revolution during the sixties and seventies and the improvement of the sediment in the Rhine water during the eighties can be recognized in these profiles for several different compounds. Depending on the degree of pollution in the Rhine water during the last decades each heavy metal shows a typical contamination pattern. The absolute amount of each compound in every time period decreases going from lake Ketelmeer to lake IJsselmeer. This dilluting factor can be explained by the fact that the IJm-deposit in lake IJsselmeer is originating also from other sources than the sediment of the river Rhine.

Table 1. Average corrected amounts of several compounds in the toplayer of the IJm-deposit and sand in both lakes.

Compounds:	Lake IJsselmeer IJm-deposit	Lake IJsselmeer sand	Lake Ketelmeer IJm-deposit
Clay-content* (%)	17	2	18
Organic Carbon* (%)	5.3	0.6	4.6
Carbonate-content* (%)	35	9.5	9.5
As (mg/kg)	15	6	24
Cd (mg/kg)	2.4	1.1	13
Cu (mg/kg)	34	8.5	124
Hg (mg/kg)	0.7	0.2	2.0
Pb (mg/kg)	60	16	160
Zn (mg/kg)	464	146	1290
EOX (mg/kg)	1.4	0.7	4.0
Oil (mg/kg)	354	330	895
Σ 7 PCBs (μg/kg)	41	19	219
Σ 6 PAHs (mg/kg)	1.9	0.6	4.7

* not corrected

INTRODUCTION TO GEOCHEMICAL GROUND WATER RESEARCH PROGRAMS BY THE U.S. GEOLOGICAL SURVEY

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Among the many agencies of the U.S. Government that have responsibilities for natural resources, the U.S. Geological Survey (USGS) is unique in that it has no enforcement, regulatory, or construction responsibilities. It is primarily a research and impartial fact-finding agency, and has been the nation's principal source of information about its physical resources. In the United States, the science of hydrology developed almost entirely within the USGS with the initiation of stream-gaging activities, regional aquifer studies, and installation of chemical laboratories. In the early years, fundamental research had to be done simultaneously with collection of basic data. By necessity the emphasis was on development of instruments, measurement and analytical techniques, and methods of interpretation.

Since its inception in 1879, the USGS has been involved in development of hydrogeologic and chemical information about water quality. The agricultural and industrial expansion after the Great Depression, stimulated in part by World War II, utilized talents of a small, but continuously increasing, cadre of water scientists who applied established hydrologic principles for development of water supplies. By the late 1950's, the demands on water scientists for evaluation for water resources and practical application to resolution of water problems were so great that research was being neglected. Therefore, to reinstitute research, as it had been in the early years, the USGS established the National Research Program. This Program encompasses a broad spectrum of scientific investigations that provide a fundamental understanding of the processes that affect the availability, movement, and quality of the nation's water resources.

By the mid-1970's the deleterious effects of contamination on ground water and surface water had become widely recognized by the public and Federal funding for research on the issues became available. Because of its sound reputation and long history of water-resources investigations, along with the recent success of the National Research Program, the USGS was the logical choice for conducting this research. Consequently, the Toxic Substances Hydrology Program was instituted and is now a major research effort. USGS studies in hydrology, chemistry, and biology provide the scientific basis necessary to investigate the complex factors that affect transport, behavior, and fate of contaminants. The seven papers in this session are examples of environmental geochemical research being done as part of these USGS programs.

COEFFICIENT OF PROPXUR PARTITION IN WATER/SEDIMENT SYSTEM

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The determination of the pesticide residue in water does not ilustrate the entire state of river and of lake water pollution.Those compounds sparingly water-soluble undergo adsorption on suspensions and sediments.Numerous authors indicated that the concentracions of pesticide residue in sediments highly escceded the quantity of those compounds in water.The mechanism and value of pesticide adsorption on sediments depends on multiple parameters, such as their specific surface,contents of silty minerals and organic substances as well as the quality of the adsobed substance.A considerable influence on the adsorption mechanism is exorted by the proton acidity of the minerals surface.The scope and speed of hydrolysis can also depend on the usable form of preparation eg.the emulsified forms can create the so called Pickering emulsion consisting in the stabilization of the emulsion particles by tiny fractions of sediments.There are frequent attemps to employ mathematical methods and computer models to the description of the environment state and the prognosis of kinetics of the pollution decomposition of the phenomena occurity in the individual elements of the system in question.This work attempts to investigate the kinetics of the adsorption of the propoxur on a sediment considency the usable form of the insecticide.The experiments were conducted on suspended Unden 50 WP and emulsified EC 200.The glass bulbs were filled with 100 cu.cm emulsion Unden 200 EC or suspension Unden 50 WP respectively,at the concentration 500 ppm. Each bulbs was added 10 g sediments.The natural sediment obtained from a river contained 35% fraction of silty minerals (below 0,02 mm),2,45% organic substance,pH equalled 6,99, and the specific surface-9,8 sq.m.The scope of adsorption was determined after 2,4,8,16 and 32 days.Qualitative analysis was based on gas - chromatography. Obtained results indicate a relatively quick achievement of the dynamic equilibrium in samples containing water suspension of Unden 50WP. After 2 days the concentration of propoxur in the sediment amounted to 3,1 ppm; further increase of the adsorbed mass was insignificant and from the 8 th day remained at the same level ie.4,5 +/-0,2 ppm. The adsorption in samples containing water emulsion of Unden 200EC was relatively slower, and the dynamic equilibrium was achieved after 16 days. Further insignificant increase of the adsorbed mass of propoxur was observed afterwards till the value 8,6 ppm was achieved.The abowe difference can be accounted for by the adsorption of the smallest particles of emulsion on the surface of sediment.The maximum adsorbed quantity of propoxur are however similar for both types of preparations (4,5 ppm for 50 WP and 5,6 ppm for 200 EC) which proves that the adsorption of the active substance (2, isopropoxy-phenyl-N-methylcarbamat) occurs mainly for the molecular solution and depends on the solubility and the adsorption capacity of the investigated sediment.

EFFECT OF WATER AERATION ON KINETICS OF PROPOXUR HYDROLYSIS

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Investigation on pesticide residue in the natural water environment indicate the durability of negative results of the application of certain insecticides which constitute a real danger for soils and waters even after their abandonment in the agricultural practice. Undissolved residues of those substances can be washed out of the soils into underground waters or rainwashed into surface waters. In particular the contamination affects small underflows and drainage ditches cutting through the intensively cultivated areas. Previous investigations on pesticide residues in the surface waters indicate the possibility of the occurence of incidentally hight concentrations manufacturing data determing the speed of pesticide decomposition in water concern the active substance itself regardless of the usable form of the preparation. The process of active substance hydrolysis should be preceeded by desorption from the suspended or emulsified preparation. The kinetics of the insecticides decomposition in water depends on the active substance type, preparation formulating means, water characteristic, etc. The investigations aimed at the kinetics of propoxur (2-isopropoxy-phenyl-N-methylcarbamat) hydrolysis based on two usable forms ie. suspended and emulsified. The bulbs of 2000 cu. cm were filled with emulsified preparation - Unden 300 EC or suspeded one -Unden 50 WP at the same concentration 500 ppm a.s. Quantitative analyses based on the water taken from the surface layer ie. containing the molecular solution of Propoxur. Such an experiment allowed for observation of the kinetics of active substance diffusion from the usable form as well as the kinetics of hydrolysis in the molecular solution. The samples for analysis were taken after 2,4,8,16 and 32 days. Qualitative analysis based on the method of gas - chromathography. To achieve this, two respectiven series of water samples each containing 100 ppm of Unden 200 EC or Unden 50 WP were prepared. One series for each usable form was aired every 8 hours over 300 min. On the basic of measurement results the kinetics curves of the successive processes of active substance release from the preparation as well as the hydrolysis were drawn. The concentration of propoxur within the molecular solution increases in the initial stage for both preparation which means that the desorption kinetics for the suspended and emulsified forms is higher than the speed of hydrolysis. The state of equilibrium for both processes occurs after 3-4 days. Since that moment that the hydrolysis starts to dominate as basic reaction of the propoxur destruction in water. After 32 days the terminating concentration of propoxur amounted to 175 ppm and 150 ppm for suspended and emulsified forms respectively. The decrease of Unden contents was always higher in the aired water as compared to the samples non-aired water. After 32 days the propoxur concentration in the non-aired water samples were for both form about 10% higher then in the aired samples.

Multielement Contamination of Soils and Plants in Old Mining Areas United Kingdom

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Soils and plants were sampled from some old Pb-Zn mining and smelting areas in England. The sampling includes natural mineralised areas, mining working places, smelter sites, and unmineralised rock-soil locations. 30 elements were analysed by ICPAES and AAS. The results show Pb, Zn, Cd, As ,Sb and Hg in soils and plants in mining and smelting sites are high elevated compared with " normal background " level, ranging in soils up to 30080 ppm Pb, 49000 ppm Zn, 375 ppm Cd, 465 ppm As, 154 ppm Sb, 5 ppm Hg; in mixed grass up to 110 ppm Pb, 192 ppm Zn, 2.06 ppm Cd, 0.46 ppm As and 0.71 ppm Sb.

The enrichment and association of the metals is affected by the following factors. (1) Parent material. The underlying mineralised rock is the main source of contamination in soils. In mineralised areas, the different stages of ore genesis produced different mineral assemblage which could control the trace element association in soils. Generally, the plant metal contents show a marked response to the increase in soil concentrations. (2) Mining activities. Mining operation and waste are the main source of heavy metals in old mining places. (3) Smelter pollution. Smelting proces have resulted in very high concentration of metals in the vicinity of smelters. The chemical form and association of metals has been shown to be different between smelting and mining areas. (4) Soil conditions, such pH, Eh, cation exchange capacity and organic matter are also important factors. The multielement associations in Pb-Zn mining and smelting areas are dominated by the presenced sulphur minerals. The typical trace element associations are in mining areas Pb-Zn-Cd-(As)-(Sb) and Zn-Cd-Pb-As-Hg-(Sb), in smelter sites Pb-Zn-(Cd)-Sb-AS.

These soil and plant results indicate that other toxic elements As, Sb, and Hg, in addition to Pb, Zn and Cd, are present as significant contaminants in the old Pb-Zn mining and smelting areas. The study of multielement associations in a typical geochemistry system can give a useful initial assessment of likely contamination in soils and plants.

BACKGROUND LEVELS AND PEDOGENIC BEHAVIOR OF TRACE ELEMENTS OF WHITE CLAY SOILS OF THE THREE RIVER PLAIN, HEILONGJIANG PROVINCE, P.R. CHINA.

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White clay soils are widely distributed in Heilongjiang Province, P.R. China and are of major agricultural and economical importance in the country. However, only little information exists on trace elements of these soils although the trace element status of soils plays an ever increasing role with the increasing concern about the quality of our environment and the increasing demand of agricultural production. Knowledge of background levels and behaviors of trace elements is essential for environmental and agricultural studies. Three representative pedons of uncultivated white clay soils in the Three River Plain, Heilongjiang Province were sampled to establish background levels of 30 trace elements and to study pedogenic behavior of these elements.

Clay separation was conducted by ultrasonic dispersion, gravity sedimentation, and centrifugation techniques. Trace elements (Ag, As, Au, B, Ba, Br, Cl, Co, Cr, Cs, Ga, Hf, I, Mn, Mo, Ni, Rb, Sb, Sc, Se, Ta, Th, U, V, W, and Zn) in both soil samples and clay separates were determined by instrumental neutron activation analysis. Contents of Ti, Zr, and Sr in soil samples were analyzed by x-ray fluorescence. Content of Hg in soil samples was measured by a flameless atomic absorption method.

New information was obtained for the background levels and pedogenic behavior of 30 trace elements for white clay soils. Current levels of these trace elements are useful for future agricultural and environmental studies. Abundance of most trace elements in this study is near the values for shale and is higher in clay separates relative to soil samples.

The geochemically inherited status of trace elements were modified by pedogenesis. There are generally five groups of trace elements recognized according to the correlation analysis and pedogenic behavior. Cl, Br, I, and Hg have an affinity for soil organic matter. Cl, Br, and I are concentrated in Ah horizons due to the input of aerosolic dust and high concentration of Hg in Ah may be the result of the coal combustion of adjacent power plants. Elements having an affinity for Mn and Fe oxyhydroxides (As, Co, and Mn) are enriched in E horizons where abundant Fe-Mn nodules occur. Elements associated with clay minerals (Cr, Rb, V, and Zn) are elevated in the bulk soil of Bt horizons. Ti, Sr, Hf, and Zr are present in relatively resistant minerals and these elements have relatively uniform profile distribution. The last group of elements include all the trace elements which were below their detection limits in one or more horizons. Consequently, there is no clear profile distribution observed for these elements.

Estimation of arsenic exposure from drinking water

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Several studies have shown that, in certain areas, As in drinking water can make a substantial contribution to the human uptake of this element. In the present study, the problem of quantifying As exposure from drinking water was investigated from statistical and chemical perspectives. Already published data sets on exposure and urinary excretion of As were reanalysed, volunteering subjects were exposed to low doses of As and a field study was performed in an area with elevated As concentrations in well water.

The experimental studies and the statistical analysis of already published data sets showed that consumption of drinking water water containing 20 - 50 ug/l of inorganic As caused an easily detectable increase of the urinary excretion of inorganic and methylated As forms. Furthermore, a three-term exponential model of absorption/excretion was found to be applicable to a wide range of doses of both trivalent and pentavalent species of As. Exposure to As via ingestion of shrimps caused a 20-fold increase in the excretion of total As, but had only a minor effect on the excretion of the more toxic inorganic and methylated As forms.

The field study of As exposure via drinking water was performed in the municipality of Smedjebacken in central Sweden, where As concentrations as high as 150 ug/l have been observed in certain wells. The distribution of different As species in well water strongly indicated that the elevated As concentrations were caused by natural leaching processes. Inorganic As(III) and As(V) species were predominant and both the total As concentration and the amount of As(III) species were positively correlated to the amount of ferrous iron. No methylated As forms were detected in any of the tested water samples. A study of 12 exposed families and a control group using drinking water of low As content showed that there was a strong correlation between As in hair and As in drinking water. There was also a strong positive correlation between the concentration of inorganic and methylated As forms in urine and As in drinking water. Further analysis of observed data showed that, even at an As concentration as low as 10 ug/l, drinking water can account for the major fraction of the exposure to inorganic arsenic.

THE SOURCES OF SULFUR OF ACID RAIN IN SOUTHWEST OF CHINA

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The city of Guiyang, located in southwest of China, is one of the areas most seriously affected by acid rain in China. From Jan. 1987 to Dec. 1989, the sulfur isotopic compositions of 113 samples of acid rain collected from Guiyang and its adjacent districts, and of many samples of atmospheric particles, coal and SO_2 released from coal-burning were determined. The results are presented as follows:

1. Acid rain is characterized as being enriched in light sulfur isotope, with all the $\delta^{34}S$ values being negative.

2. The $\delta^{34}S$ values of acid rain samples show regular fluctuations or continuous seasonal variations. In other words, the $\delta^{34}S$ values decrease from the maximum in January or February to the minimum in June or July, and then tend to increase gradually (Table 1).

Table 1. Monthly Average $\delta^{34}S$ Values of Acid Rain (‰)

Y \ M	J	F	M	A	M	J	J	A	S	O	N	D
1987	—	-4.41	—	-1.92	-6.23	-5.27	-7.16	-5.59	-4.91	-5.49	-5.13	-5.41
1988	-2.17	-1.90	—	-3.46	-6.07	-6.47	-6.97	-6.74	-6.15	-7.85	—	-2.41
1989	—	-3.31	-3.76	-6.36	-8.70	-9.44	-10.23	-6.41	-7.32	-6.38	-5.78	-6.28

3. According to the principle of isotopic mass balance, five sources of sulfur are distinguished for acid rain (Table 2).

ORIGIN OF MERCURY ACCUMULATION IN BLACK SPRUCES FROM CANADIAN BOREAL FOREST

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Total mercury accumulation in trees - the bark, leaves, and wood situated at different geographic orientations on the tree - and the soils surrounding the tree roots were sampled in the Canadian boreal forest at two stations about 700 km apart. The southern station was closer to industrial sources than the northern and had older trees. Mercury concentration in the different parts of the trees were between 2 and 145 ng/g and in the soils between 18 and 115 ng/g. The highest mercury concentration was found in the soils of the southern and in the bark of the northern station. Our results also show that mercury accumulation in the tree-rings appears dependent on the geographic orientation.

The differing mercury concentrations found in the various measured compartments, and between stations, will be analysed in relation to local variables (tree-growth, soil characteristics, precipitation, frequency of fire, ...) and long range transport of pollutants.

Geochemical Characteristics of Element distributions in waters of the Yangtze River

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Abstract

Yangtze River is the longest river in China and the third longest river in the world. The eco-environmental conditions of the Yangtze River is very complicated and various. From 1987 to 1990, comprehensive geochemical investigation to the aquatic environment in this area was conducted. The natural contents and background values of Cu, Pb, Zn, Cd, Hg, As, Co, Ni, Cr, Se, Mn, Mo, Fe, V, F, Sr, Ba, Rb, Ce, U, Sc etc. in waters were obtained. It was found that:

1. There are great differences in the contents of these elementsin waters of the Yangtze River, but the contents of these elements in most sample sites tended to a definite amount.

2. The background values of these elements in unfiltered and filtered water are in a low level compared to the values in other rivers of china and abroad.

3. The contents of most elements in soluble form acount for a higher proportion of total amounts of these elements compared to the results of other rivers of china and abroad. F, Se, Ni, Hg, Sr, Ba, U mainly exsist in soluble form, whereas Fe, Mn, Cr, As, Rb, Sc, Th, La, Ce mainly associated with suspended particles.

4. There exsits distinct area variation in the contents of trace elements in waters of the Yangtze River.

High Concentrations of Arsenic in Groundwaters in the Mid-Lower reaches of Yangtze River Riparian, China

Abstract

High concentrations of Arsenic in groundwaters(HCAG) occur in many places, such as Wuhan, Nanjing, Yangzhou, Nantong, and Shanghai cities, along the mid-lower reaches of Yangtze River riparian, China. Residents cannot drink the waters brcause Arsenic concentrations exceed the sanitary standard of drinking water, and adversely affect human health.

HCAGin the reports are associated with geochemical environments. The waters exist in the Quanternary unconsolidated aquifers, basin-fill deposits of alluvial origin, in the turtuous or intersection of the river geomorphologically, in the confined or quasi-confined aquifers hydrodynamically. Arsenic contains in phreatic and/or artisian waters in the deeper aquifer are not high in the places where HCAG occur.pH and Eh values tested in situ indicate that HCAG occur in the reduction environments. HCAG occurrence are almost together with high concentrations of Fe^{2+} and Mn.

Arsenic in groundwaters originates from arsenic sissolution in the water-bearing media. The background values of arsenic in the water-bearing media range between 1.0--40.0 mg/kg, increasing with fine-grain size sediments toward the lower reaches of the river, and with rich of organic matter and iron and manganese oxides.

Experiment shows that seawater is of maxisum capable of disolving arsenic from the water-bearing media, which is the reason why HCAG occur in Nantong area where marine transgres - sion happened during the Pleistocene period. Arsenic in groundwaters can be attenuated through aeration tank, chemical precipitation and other methods.

Zhou Hongchun (China University of Geosciences)

CHEMICAL WEATHERING IN THREE ACID SULFATE SOILS IN SWEDEN

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The extremely acidic conditions in acid sulfate soils provide a good opportunity to study the effects of chemical weathering on soil chemistry and mineralogy under field conditions. The K-fixation capacity, total elemental composition, and mineralogy (0.2-2um fraction) of three cultivated acid sulfate soils in Sweden were investigated. The study was mainly based on comparisons between the Bwg and Cr horizons. The time elapsed since the sulfides were oxidized was estimated at 100 years for the Sörby soil, fine, mixed(acid), frigid Histic Humaquept, 450-600 years for the Ängesbyn soil, fine-silty, mixed(acid) Aeric Humic (Sulfic) Cryaquept, and 1100-1600 years for the Bro soil, very-fine, mixed(acid), frigid Humic (Fluvaquentic) Haplaquept.

The K-fixation capacity, used as an early indicator of weathering, was higher (at least dubbled) in the Bwg horizons than in the Cr horizons in each of the three studied soils. Recalculated in relation to clay content the difference in K-fixation between the horizons was highest in the Cryaquept, which had the lowest clay content. The mineralogical study (XRD) of the coarse clay fraction indicated that vermiculites and vermiculite-containing mixed-layer minerals had been formed from micas as well as chlorites, mainly in the two older soils but also to some extent in the younger one. Elemental losses were estimated using Si as internal standard. Mn (15-46%) and Mg (10-33%) were lost in all three soils, and Ca (20-24%) in two soils. In conclusion my findings indicate that loss of elements was rather fast during the sulfur oxidation and that alterations of the clay minerals (XRD) were more pronounced in the older soils.

LEAD ISOTOPES AS TRACERS OF POLLUTION FROM MINING INDUSTRIES

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The element lead has four stable isotopes. ^{206}Pb is formed by the radioactive decay of ^{238}U, ^{207}Pb from ^{235}U, ^{208}Pb from ^{232}Th and ^{204}Pb is non-radiogenic. The metal lead is produced from the mineral galena, PbS. Since galena contains no uranium or thorium, the lead isotopic composition usually has not changed since the ore formation. Lead-bearing silicates, on the other hand, contain both uranium and thorium which results in a continuous change of the isotopic composition. Further, lead derived by radioactive decay occupies defect lattice positions in silicates and is liberated by weathering in preference to the original lead. This results in that lead ores, and recent sediments derived from rocks of the same age as the ores, could have different isotopic compositions. Even if different geological formations in a certain area have different isotopic compositions, it is probable that a recent unpolluted sediment in this area has a relatively constant isotopic composition since the various components of the sediments have been homogeneously mixed. In an area with mining activities, it is thus possible to quantify the lead pollution with a simple mixing-model.

In the Bergslagen mining district in south central Sweden, numerous mines were in production already during the medieval period. Several mines are still in production. The River Dalälven flows throuh Bergslagen, and the river is contaminated by acid mine drainage. Major elements, trace elements and lead isotopes were analysed in sediments from Dalälven. The sediment samples were taken from the sediment surface down to a depth of 39 cm. The ores in Bergslagen are c. 1.9 Ga old, and the ore lead has a very homogeneous composition with the average ratios $^{206}Pb/^{204}Pb = 15.72$, $^{207}Pb/^{204}Pb = 15.36$ and $^{208}Pb/^{204}Pb = 35.21$ (Billström, 1989). Corresponding background ratios for unpolluted sediments are 23.49, 16.72 and 42.09. The background concentration of lead in the sediments is c. 20 ppm. The surface sediments contain between 160 and 220 ppm lead, which according to the mixing model based on isotopic ratios correspond to c. 72 % ore lead and 28 % bakground lead. The highest lead concentrations have been found at a depth of 2-3 cm at one sample station (477 ppm, 74 % ore lead), and at a depth of 9-12 cm at another station (572 ppm lead, 82 % ore lead) which thus appears to have faster sedimentation rate. Since the surface sediments are less contaminated with ore lead than the sediments a few cm down, it is probable that the pollution rate has decreased from its maximum value. This is supported by the results that the lead isotope ratios of both the river water and the suspended particles in the river are almost the same as those of the surface sediments.

Another important mining area in sweden is the so-called Skellefte sulphide ore district in northern Sweden. The ores are of approximately the same age as those in Bergslagen, but most of the lead processed in the smelter Rönnskärsverken close to Skellefteå is c. 600 Ma old and comes from the Laisvall mine. Both the Skellefte district ores and the Laisvall ore have well-defined ratios of lead isotopes. To study if the sediments in the Bothnian Bay have been contaminated with metals from Rönnskärsverken or from smelters in Finland, we have analysed sediment samples for major elemnts, trace elements and lead isotopes. These results will also be presented.

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