

# Sällsynta jordartsmetaller i Sverige, förekomst och utbredning i berg och jord

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Uppdatering av texten i inledningen.  
Ändring av radbrytning i tabell 7.

Omslagsbild: Gadolinit från Ytterby.  
Foto: K.-E. Alnavik.

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## SAMMANFATTNING

Det finns flera faktorer som kontrollerar fördelning och koncentrationer av sällsynta jordartsmetaller (REE) i jord. Utbredningen av sällsynta jordartsmetaller i norra respektive södra Europa är tydligt påverkad av variationer i geologi och klimat. Jordens surhetsstatus samt närvaron av kalkpartiklar och organiskt material är faktorer som påverkar koncentrationen av sällsynta jordartsmetaller i ytlig jord (topsoil) i förhållande till ursprungsmaterialet i underliggande jord (subsoil). Sverige har lägre halter av sällsynta jordartsmetaller i ytlig jord än i underliggande jord, vilket sannolikt beror på en urlakning av metallerna i det sura, humusrika skikt som täcker den underliggande jorden. Förhållandet är helt motsatt i t.ex. Italiens varma klimat, där välkomposterad, vittrad jord utgör ytlig jord, ofta med ett innehåll av kalk. De högsta halterna av cerium, lantan och yttrium i Europa är kopplade till den lerrika jord som utvecklats över karst (terra rossa). Även det centraleuropeiska lössbältet har förhöjda koncentrationer liksom det centralskandinaviska lerbältet. Höga koncentrationer i jorden förklaras av affiniteten hos sällsynta jordartsmetaller att bindas till kalciummineral i samband med magmatiska processer och att adsorbera till lerpartiklar.

Spridningsmönstren för sällsynta jordartsmetaller visar att alkaliska jordar med högt pH tenderar att vara anrikade på dessa metaller. Till exempel har karbonatiska jordar högre koncentrationer av dessa element. I norra Europa, norr om gränsen för inlandsisens maximala utbredning, är koncentrationerna av sällsynta jordartsmetaller låga utom för den Skandinaviska halvön. I denna region speglar elementens uppträdande antingen kristallin berggrund, som i stora delar av Sverige, eller marina, lerrika sediment, som i centrala Sverige och södra Finland.

Spridningsmönstren med lantan-, cerium- och yttriumanomalier över Europa korrelerar i hög grad med kända förekomster av fosfatmineraliseringar, till exempel i Italien, Skandinavien, Spanien och England.

## **SUMMARY**

There are several factors that control the distribution and concentration of rare earth elements (REE) in the soil. The distribution of REE in northern and southern Europe is clearly influenced by variations in geology and climate. Acidity in the soil and the presence of carbonate and organic matter are factors that affect the REE concentration in surface soil (topsoil), relative to the origin of the material in the underlying soil (subsoil). Sweden has lower REE concentrations in topsoil than in subsoil, which is probably due to leaching of metals in the acidic, humus-rich layer that covers the subsoil. The situation is completely opposite in, for instance, Italy's warm climate, where decomposed, weathered soil constitutes topsoil, often with a content of carbonate. The highest concentrations of cerium, lanthanum and yttrium in Europe relate to the clay-rich soil developed over karst (*terra rossa*). The Central European loess belt has elevated REE concentrations as well as the central Scandinavian clay belt. High concentrations in the soil are explained by the affinity of rare earth elements to bind to calcium minerals in igneous processes and to adsorb to clay particles.

Distribution patterns of REE show that alkaline soils of high pH tend to be enriched in rare earth elements and, as an example, carbonate rich soils have higher concentrations of these elements. In northern Europe, north of the maximum extent of the Weichselian ice sheet, the concentrations of REE are low except in the Scandinavian Peninsula. In this region, the elements reflect either the presence of crystalline bedrock, as in large parts of Sweden, or marine, clay-rich sediments, as in central Sweden and southern Finland.

The distribution patterns of lanthanum, cerium and yttrium of Europe correlate strongly with known occurrences of phosphate mineralisation, for example in Italy, Scandinavia, Spain and Great Britain.

## INLEDNING

Huvudsyftet med detta projekt har varit att sammanställa grundläggande fakta om sällsynta jordartsmetaller (rare earth elements, REE), att ta fram statistik över kemiska analysresultat för sällsynta jordartsmetaller i jord och berg i Sverige, att presentera dem på kartor och att belysa deras geogena relevans.

I dagsläget står Kina för 75 % av världsproduktionen av sällsynta jordartsmetaller vilket gör att EU har ett stort importbehov av sällsynta jordartsmetaller (ERACON 2014). Behoven av metallerna ökar i takt med den ökande högteknologiska utvecklingen och med miljövänlig energiförsörjning. De sällsynta jordartsmetallerna är strategiskt viktiga, och de ingår i EUs lista över kritiska metaller och mineral för vilka Europa måste sträva efter att minska beroendet av utländsk produktion genom att söka nya mineralförekomster.

Den svenska berggrunden bedöms ha goda förutsättningar för att innehålla ekonomiskt brytvärda kvantiteter av sällsynta jordartsmetaller. Ett exempel i Sverige är fyndigheten Norra Kärr vid Vätterns östra strand. Denna förekomst är intressant både för sin beräknade mineraltillgång och för det faktum att halterna av uran och torium, vilka förekommer tillsammans med de sällsynta jordartsmetallerna, är mycket lägre än i andra förekomster i Sverige, Europa eller på andra håll i världen. De är dessutom lägre än omgivande bergarter.

För denna rapport har vi använt databaserna FOREGS (Forum of European Geological Surveys, subsoil och topsoil), GEMAS (Geochemical mapping of agricultural and grazing land soils, åkermark och betsmark), Geokemisk atlas över Sverige, (morän) och SGUs litogeokemiska databas. Vi har också använt resultat som publicerats i vetenskapliga artiklar (Bilaga 1), i bokkapitel (Andersson m.fl. 2014) och som abstrakt i samband med vetenskapliga konferenser och möten (Sadeghi m.fl. 2012, Sadeghi m.fl. 2013c, Sadeghi m.fl. 2014).

Historiken om de sällsynta jordartsmetallernas upptäckt börjar i slutet av 1700-talet då man i Ytterby gruva utanför Vaxholm i Stockholms skärgård fann ett svart mineral med dittills okända grundämnen i pegmatit. I Ytterby pegmatitbrott bröts kvarts och fältspat som användes för tillverkning av porslin av fabrikerna Rörstrand och Gustavsberg. Den svenska kemisten Johan Gadolin var den som i det svarta mineralet upptäckte grundämnet yttrium år 1794. Mineralet fick senare namnet gadolinit efter honom (Enghag 1999).

I Västmanland finns Riddarhyttans malmfält som omfattar en stor mängd större och mindre gruvområden där järnmalm började brytas för nästan tusen år sedan. Huvudsakligen var det järn och koppar som utvanns, men det fanns också förekomster med kobolt och molybden. I Bastnäsfältet, i östra delen av Riddarhyttans utbredda malmfält, kom gruvbrytningen igång redan i mitten av 1300-talet vilket gör det till ett av de äldsta malmfälten i Sverige. I den nyare delen av Bastnäsfältet finns Ceritgruvan och S:t Görans koppargruva som båda brutits på cerit, men även allanit har utvunnits (Öhman m.fl. 2004).

Upptäckten av cerium i ett rött mineral från Bastnäsfältet tillskrivs Jöns Jakob Berzelius, en svensk kemist som 1803 upptäckte den första av de sällsynta jordartsmetallerna i mineralet bastnäsit. Det dröjde till år 1839 innan ytterligare en svensk, Carl Gustav Mosander, upptäckte lantan. Samma år fann Axel Erdmann lantan i mineralet mosandrit från Norge. Fler upptäckter från Bastnäs är praseodym och neodym (båda 1885).

I Ytterby gruva upptäcktes erbium (1843) och terbium (1878) av Carl Gustav Mosander. I samma gruva har man också hittat ytterbium (1878), samarium och skandium (båda 1879). Svensken Per Teodor Cleve fann holmium och tulium år 1879. Upptäckten av gadolinium gjordes 1880, dysprosium 1886, europium 1896, lutetium 1907 och slutligen prometium 1945.

Att metallerna kallas sällsynta beror på att de mineral de ingår i inte är särskilt vanliga och att de sällan bildar egna mineral. Metallerna ingår mer frekvent i bergartsbildande mineral och sällsynta jordartsmetaller förekommer i jordskorpan i högre grad än till exempel koppar och bly.

Tabell 1. Spearmans korrelationsmatris för sällsynta jordartsmetaller, skandium och yttrium. LREE respektive HREE är inramade.

N=2578	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Sc	1,0	0,6	0,5	0,6	0,6	0,6	0,6	0,6	0,6	0,5	0,5	0,5	0,4	0,4	0,4	0,5
La	0,6	1,0	0,9	1,0	1,0	0,9	0,6	0,8	0,8	0,7	0,6	0,6	0,5	0,5	0,5	0,6
Ce	0,5	0,9	1,0	0,9	0,9	0,8	0,6	0,8	0,7	0,7	0,6	0,6	0,5	0,5	0,5	0,6
Pr	0,6	1,0	0,9	1,0	1,0	1,0	0,6	0,9	0,8	0,8	0,7	0,6	0,6	0,5	0,5	0,7
Nd	0,6	1,0	0,9	1,0	1,0	1,0	0,6	0,9	0,9	0,8	0,7	0,6	0,6	0,5	0,5	0,7
Sm	0,6	0,9	0,8	1,0	1,0	1,0	0,6	1,0	0,9	0,9	0,8	0,7	0,7	0,6	0,6	0,8
Eu	0,6	0,6	0,6	0,6	0,6	0,6	1,0	0,6	0,6	0,6	0,6	0,6	0,5	0,5	0,5	0,5
Gd	0,6	0,8	0,8	0,9	0,9	1,0	0,6	1,0	1,0	0,9	0,9	0,8	0,7	0,7	0,7	0,8
Tb	0,6	0,8	0,7	0,8	0,9	0,9	0,6	1,0	1,0	1,0	0,9	0,9	0,8	0,8	0,8	0,9
Dy	0,5	0,7	0,7	0,8	0,8	0,9	0,6	0,9	1,0	1,0	1,0	1,0	0,9	0,9	0,9	0,9
Ho	0,5	0,6	0,6	0,7	0,7	0,8	0,6	0,9	0,9	1,0	1,0	1,0	1,0	0,9	0,9	1,0
Er	0,5	0,6	0,6	0,6	0,7	0,6	0,6	0,8	0,9	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Tm	0,4	0,5	0,5	0,6	0,6	0,7	0,5	0,7	0,8	0,9	1,0	1,0	1,0	1,0	1,0	0,9
Yb	0,4	0,5	0,5	0,5	0,6	0,6	0,5	0,7	0,8	0,9	0,9	1,0	1,0	1,0	1,0	0,9
Lu	0,4	0,5	0,5	0,5	0,6	0,6	0,5	0,7	0,8	0,9	0,9	1,0	1,0	1,0	1,0	0,9
Y	0,5	0,6	0,6	0,7	0,7	0,8	0,5	0,8	0,9	0,9	1,0	1,0	0,9	0,9	1,0	

De sällsynta jordartsmallerna omfattar 15 lantanoider med atomnummer från lantan (57) till lutetium (71). De är kemiskt lika och återfinns huvudsakligen i samma geologiska miljöer. Metallgruppen delas in i två undergrupper: de lätta jordartsmallerna (light rare element group, LREE) och de tunga (heavy rare element group, HREE). Den lätta gruppen har atommassor från 138,91 u till 151,96 u (unified atomic mass unit) och omfattar lantan (La), cerium (Ce), praseodym (Pr), neodym (Nd), prometium (Pm), samarium (Sm) och europium (Eu). Den tunga gruppen har atommassor från 157,25 u till 174,97 u och omfattar gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), tulium (Tm), ytterbium (Yb) och lutetium (Lu). Yttrium (Y) med atomnummer 39 räknas traditionellt in i REE-gruppen på grund av liknande geokemiskt och fysikaliskt uppträdande och särskilt till undergruppen tunga jordartsmallarer (Hu m.fl. 2006). Även skandium (Sc, atomnummer 21) brukar knytas till de sällsynta jordartsmallerna och då till den lätta gruppen.

De lätta jordartsmallerna cerium och lantan är de två vanligast förekommande i REE-gruppen, och de har också högst halter i jordskorpan. Metallerna i den tunga gruppen har generellt betydligt lägre halter och är inte alltid detekterbara i vanliga analysen. Sådana är optimerade för att ge data för grundämnen med ett brett koncentrationsintervall, och för att möjliggöra det är detektionsgränserna i regel höga. Yttrium förekommer dock med högre halter i jord och berg, vilket gör analyser av yttrium till en bra indikator för de tunga jordartsmallerna. Cerium, lantan och yttrium är därför nyckelelement för de sällsynta jordartsmallernas uppträdande (McLennan 1989, Sadeghi m.fl. 2013a, 2013b). Det finns en stark koppling mellan metallerna, vilket visar sig t.ex. i korrelationsmatrisen för metallerna i morän (tabell 1). Till matrisen har vi använt analysresultat för metallerna i kungsvattenlakad morän <0,063 mm, från Geokemisk atlas över Sverige .

## SÄLLSYNTA JORDARTSMALLER I BERGGRUND OCH MINERALISERINGAR

Sällsynta jordartsmallar förekommer generellt associerade till primära och sekundära geologiska processer. Primära förekomster associeras till magmatiska och hydrotermala processer medan sekundära förekomster har bildats genom sedimentation och vittring. Sällsynta jordartsmallar förekommer generellt i magmatiska bergarter, huvudsakligen granitoider och alkalina

Tabell 2. Mineralgrupper med innehåll av viktiga sällsynta jordartsmetaller (REE), skandium och yttrium.  
Modifierad efter International Mineralogical Association (IMA).

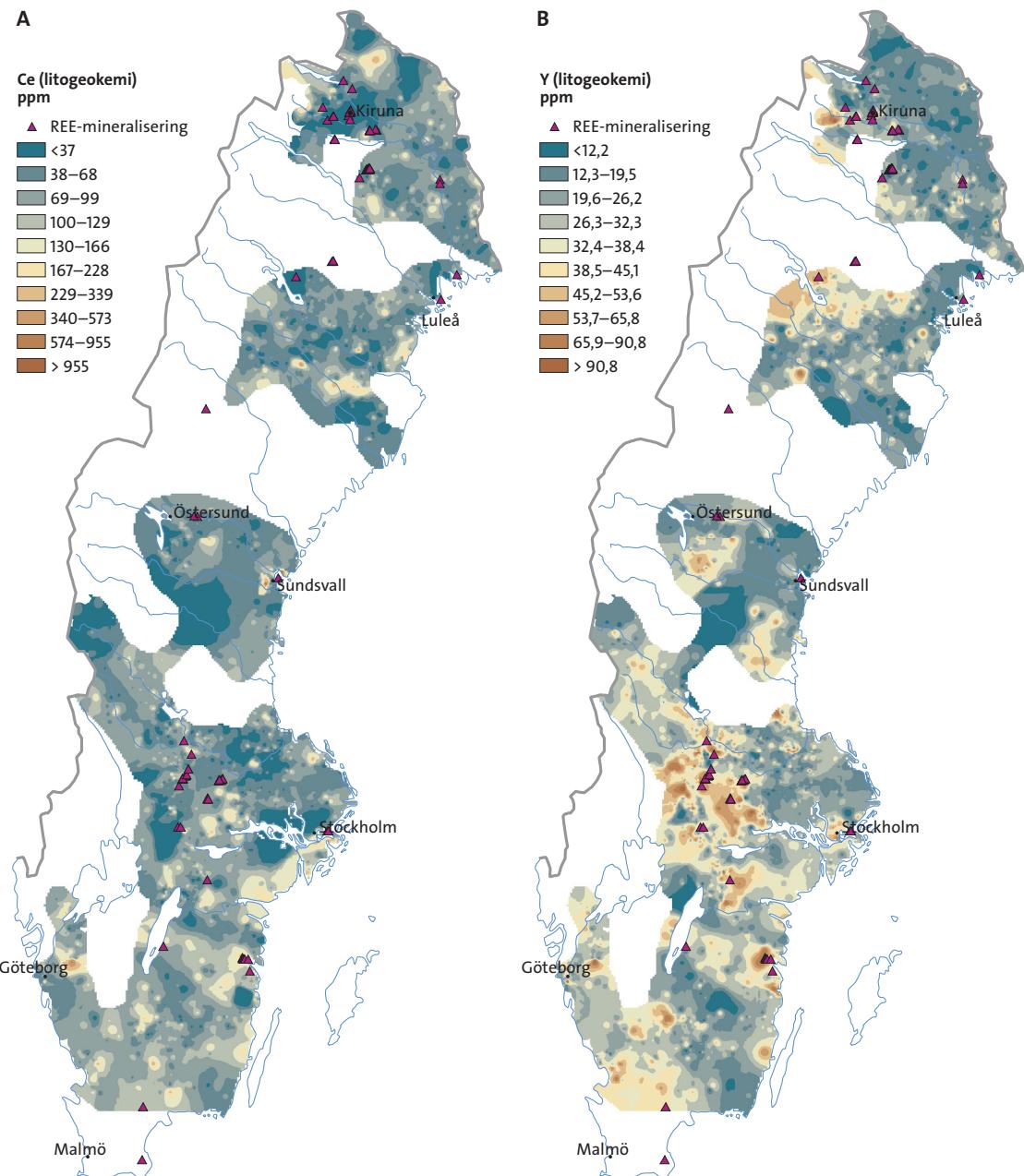
Mineralgrupp	vanligaste REE	Mineralgrupp	vanligaste REE
Ankylitgruppen	Ce, La, Nd	Lantanitgruppen	Ce, La, Nd
Apatitgruppen	Ce, La	Monazitgruppen	Ce, La, Nd
Bastnäsitgruppen	Ce, La	Mosandritgruppen	Ce, La
Britolitgruppen	Ce, La	Norditgruppen	Ce, La
Chevkinitgruppen	Ce, La	Parisitgruppen	Ce, La
Crandallit-(alunit-jarosit)-gruppen	Ce, La, Nd	Pyroklorgruppen	Ce, Y
Donnayitgruppen	Nd, Y	Remonditgruppen	Ce, La, Nd
Epidotgruppen	Ce, La, Nd	Samariskitgruppen	Y, Yb, HREE
Eudialytgruppen	REE, Y	Synchysitgruppen	Ce, Nd, Y, La
Euxenitgruppen	Ce, Y	Thortveititgruppen	Sc, Y, Yb
Gadolinit-datolitgruppen	Ce, Nd, Y	Trimounsitgruppen	Dy, Er, Yb, Y
Gagarinitgruppen	La, Nd, Y	Tritomitgruppen	Y, Ce
Hellanditgruppen	Ce	Uraninitgruppen	Ce, La
Hilairitgruppen	Gd, Dy, Y	Wöhleritgruppen	Y
Kordylitgruppen	Ce, La	Xenotimgруппen	Y, Yb, HREE, Ce
Kukharenkoitgruppen	Ce		

bergarter. Sedimentära bergarter som sandsten och kalksten har ett lågt innehåll av sällsynta jordartsmetaller, men skiffrar och gråvackor kan ha ett högre innehåll. Sällsynta jordartsmetaller har affinitet för syre och förekommer företrädesvis i sedimentära bergarter som fosforit och argillit. Bergarter som är anrikade på monazit och zirkon har alltid förhöjda halter av sällsynta jordartsmetaller.

SGUs litogeokemiska databas innehåller omkring 14 000 bergartsanalyser, men det finns bara ca 5 700 analyser av sällsynta jordartsmetaller. Databasen är under uppbyggnad och inte helt homogen vad avser kvalitet. Preliminära kartor baserade på litogeokemiska data visar överstående variationen av sällsynta jordartsmetaller i berggrunden där det finns analyser. Vi har tagit fram kartor över Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y och Yb. Kartorna i figur 1 visar exempel från både den lätta gruppen (fig. 1A, Ce, LREE) och den tunga gruppen (fig. 1B, Y, HREE). Övriga kartor finns i Bilaga 2.

Lantan (och de lätta jordartsmallerna, LREE) uppträder som spårelement i bergartsbildande mineral som är mer vittringsbegäna och har något högre mobilitet än yttriumbärande mineral. Lantan finns i flera vanliga bergartsbildande mineral som glimmer och fältspat samt i accessoriska mineral som monazit. Yttrium förekommer huvudsakligen i vittringsresistenta accessoriska mineral som zirkon och xenotim. Därför förekommer lantan i betydligt högre halter i granit än vad yttrium gör. Yttrium och de tunga jordartsmallerna (HREE) bildar stabilare komponenter än vad lantan och de lätta jordartsmallerna (LREE) gör vilket gör att den tunga metallgruppens mobilitet är låg i den naturliga miljön.

De sällsynta jordartsmallerna bildar ett flertal mineral. De vanligaste är monazit, bastnäsit, allanit och cerit. Sällsynta jordartsmallar ingår i karbonater, oxider, silikater, fosfater och halider, och kan finnas i exempelvis apatit, biotit, pyroxen, turmalin och zirkon. Kalcium-mineral, och då särskilt bergartsbildande mineral som hornblände, augit, apatit och fluorit, binder sällsynta jordartsmallar i samband med magmatiska processer och hydrolys (Liu 1988). Metallerna, särskilt ur den lätta gruppen (LREE), kan förekomma i fluorit samt ersätta kalcium i fältspat. Det finns omkring 200 mineral som innehåller sällsynta jordartsmallar. I en del mineral domineras LREE över HREE, i andra är förhållandet det motsatta. I tabell 2 är några vanliga mineralgrupper listade tillsammans med de kommersiellt viktigaste sällsynta jordartsmallerna samt skandium och yttrium.

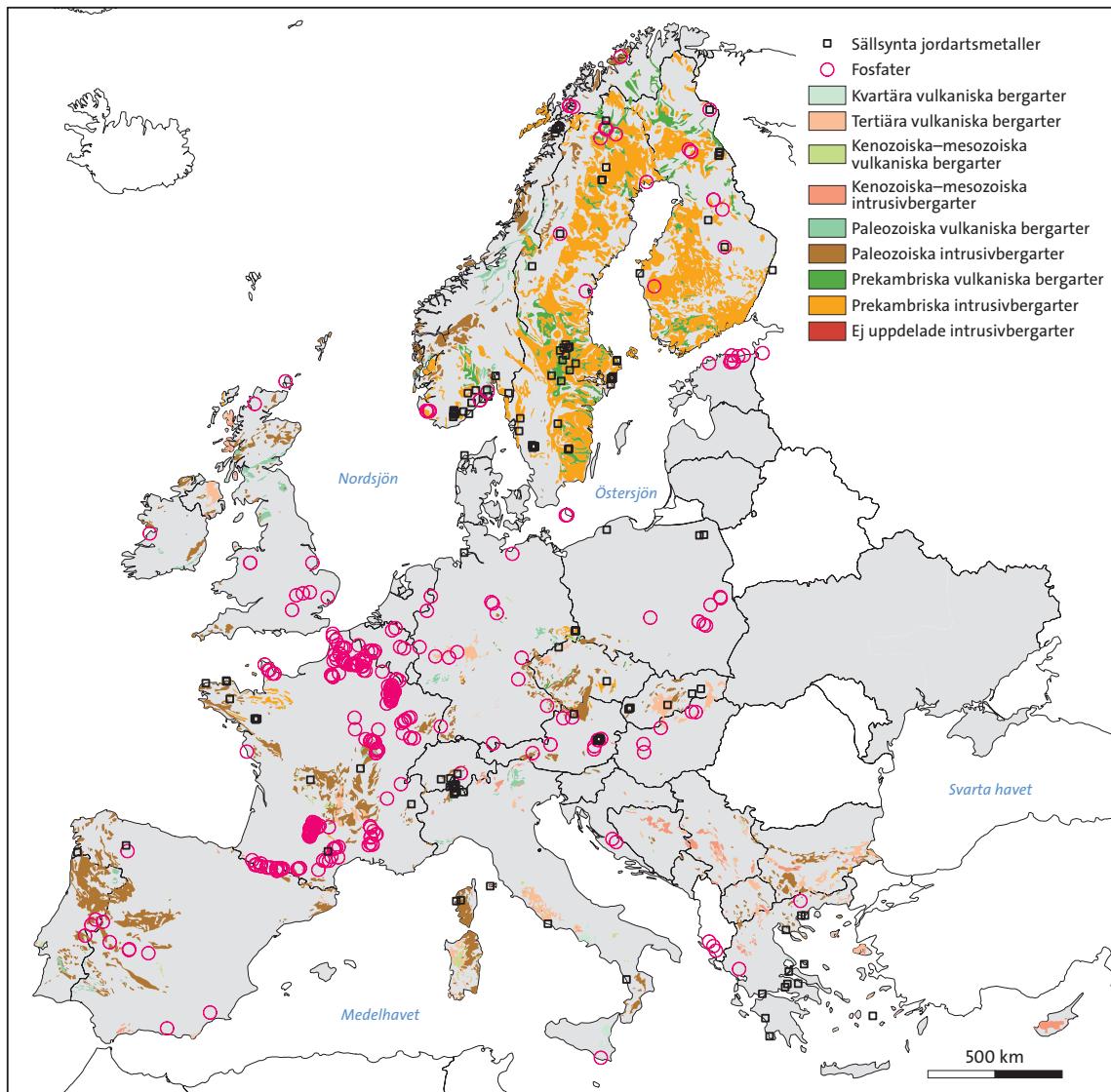


Figur 1. A. Cerium (Ce) i berggrunden. B. Yttrium (Y) i berggrunden. Trianglarna markerar ett urval kända mineraliseringar med sällsynta jordartsmetaller.

Kartan i figur 2 (se även Bilaga 1) visar ett urval av mineralresurser i Europa med fokus på sällsynta jordartsmetaller och fosfat, och den är baserad på databaser från Promine ([www.promine GTK.fi](http://www.promine GTK.fi)) och FODD (<http://geomaps2 GTK.fi/website/fodd/viewer.htm>).

Kända förekomster med sällsynta jordartsmetaller i Sverige kan delas upp i sju karakteristiskt skilda metallogenetiska kategorier som gett upphov till mineraliseringar med sällsynta jordartsmetaller (fig. 3, se även Bilaga 1). Mineraliseringarna skiljs åt genom sin tektoniska historia och geokemiska karaktär, och de olika kategorierna känns huvudsakligen igen som mineraliseringar av

- sällsynta jordartsmetaller tillsammans med apatitjärnmalm,
- hydrotermal Bastnästyp (järnoxid-Cu-REE),

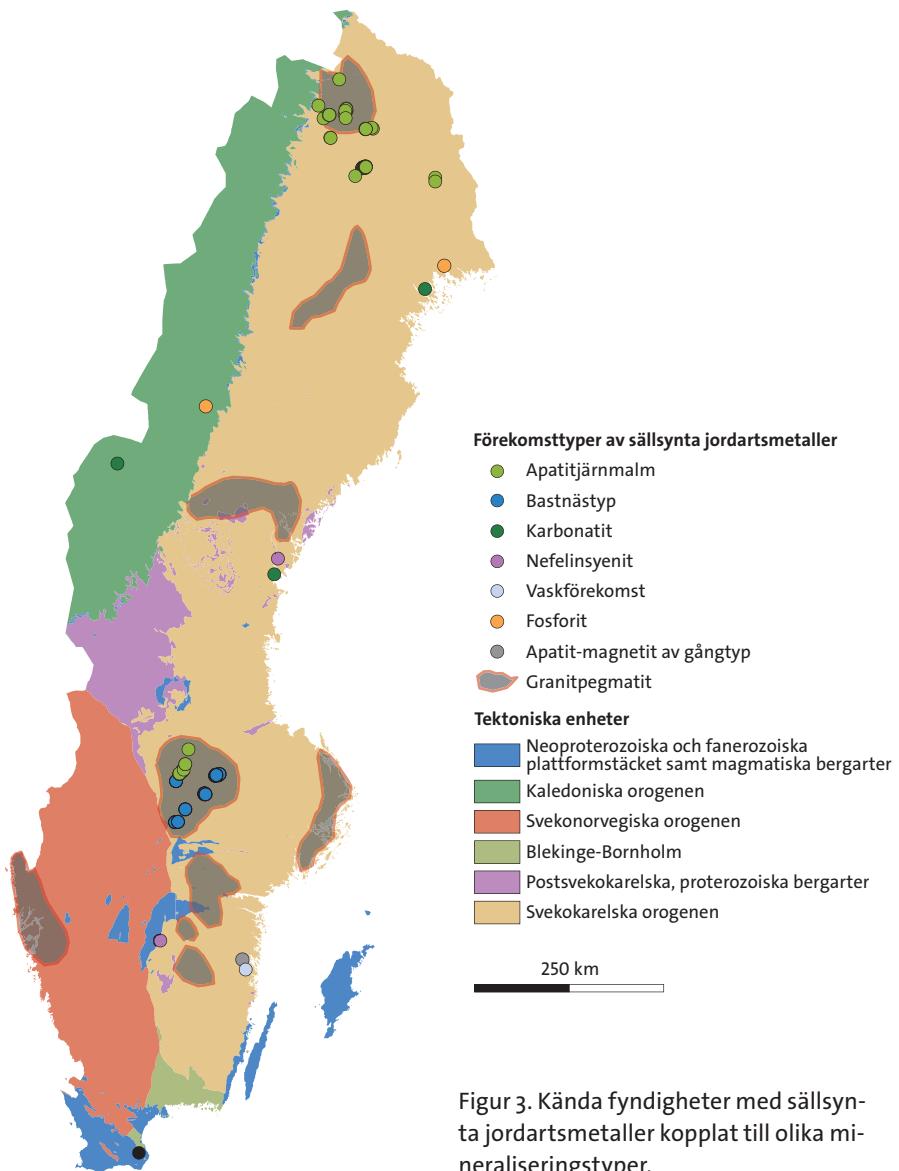


Figur 2. Utbredning av vulkaniska och magmatiska bergarter tillsammans med kända förekomster av sällsynta jordartsmaller och fosfat. Området motsvarar GEMAS-projektets areal.

- sällsynta jordartsmaller relaterade till alkalina komplex med karbonatit,
- sällsynta jordartsmaller i peralkalin nefelinsyenit,
- sällsynta jordartsmaller som vaskavlagringar i kvartsit,
- sällsynta jordartsmaller i pegmatit,
- sällsynta jordartsmaller med uranrik fosforit.

I Norrbotten och centrala Sverige förekommer sällsynta jordartsmaller i apatitjärnmalm, t.ex. Kiruna och Malmberget i norr och Grängesberg i västra Bergslagen. Förekomster av Bastnästyp finns i Bergslagen i Bastnäs gruvor i Riddarhyttefältet och sydväst därom. Tillsammans med koppar och järn finns ceriumrika partier som tagits tillvara i samband med brytning av malmen.

I en tektonisk svaghetszon som sträcker sig från Halland i sydväst längs Bottenvikens kust till Kalix i norra Sverige och vidare över Finland till ishavet vid Kolahalvön finns förekomster



Figur 3. Kända fyndigheter med sällsynta jordartsmetaller kopplat till olika mineraliseringstyper.

kopplade till karbonatit (Kalix, Åviken och Alnön) och nefelinsyenit (Särna, Almunge och Norra Kärr i Östergötland).

I närheten av Västervik uppträder sällsynta jordartsmetaller i kvartsit och i Tåsjöområdet i fosforitförande skiffer. I en kvartsitisk gnejs vid Olserum förekommer sällsynta jordartsmetaller i gångar med apatit och magnetit, och i sydöstra Skåne i fluoritförande gångar i kvartssandsten. Pegmatit som innehåller mineral med sällsynta jordartsmetaller förekommer på ett flertal platser över hela landet.

## SÄLLSYNTA JORDARTSMETALLER I JORD OCH ANTROPOGENA KÄLLOR

Koncentrationen av sällsynta jordartsmetaller i jordar beror bland annat på jordens fysikaliska och kemiska karaktär samt olika markprocesser som adsorption eller desorption (Ran & Liu 1993), pH (Dong m.fl. 2001), närvaro av organiskt material (Beckwith & Butler 1993) och tiden det tar att nå jämvikt vid hydrotermala processer (Li m.fl. 2000). De sällsynta jordarts-

metallernas mobilitet varierar beroende på deras mineraltillhörighet och därfor varierar också koncentrationen av sällsynta jordartsmetaller i jord (Hu m.fl. 2006). I jordar förekommer sällsynta jordartsmetaller till stor del som karbonater och det har därfor funnits förslag hos en del forskare (Zhu & Xing 1992) att karbonatbundna sällsynta jordartsmetaller skall klassas som en oberoende form av sällsynta jordartsmetaller. Höga koncentrationer av sällsynta jordartsmetaller i Europa finns i områden med kalkrik berggrund, men också med basiska vulkaniter och vissa graniter.

Generellt är koncentrationerna av sällsynta jordartsmetaller högre i Balkanländerna och Medelhavsländerna vilket kopplas till ett starkt inflytande av varmt klimat och sekundär anrikning av sällsynta jordartsmetaller i jordarna (Petrosino m.fl. 2013). Historiskt sett har klimatet med vittring och erosion spelat en stor roll i södra Europa och i Medelhavsregionen med utveckling av residuala jordar (t.ex. terra rossa) som har ett högt innehåll av sällsynta jordartsmetaller. I dessa områden (Italien, Grekland, Cypern, Portugal, Ungern, Kroatien) finns höga koncentrationer av sällsynta jordartsmetaller i t.ex. betesmark, där lerrika lager med järnoxider har utvecklats i jordar som inte blivit omstrukturerade genom plöjning.

Lokalt bergartsmaterial är normalt den vanligaste källan till sällsynta jordartsmetaller i jordar, men nya användningsområden i samhället förväntas öka den antropogena cirkulationen av metallerna. Ökad industriell användning av sällsynta jordartsmetaller med spridning till miljön kan potentiellt orsaka hälsoeffekter på människor och djur (Hirano & Suzuki 1996, Haley 1991). Utöver oavsiktlig spridning av sällsynta jordartsmetaller vid gruvbrytning kan även elektroniskt avfall ge upphov till föroringningar (Haxel m.fl. 2002). Oljeraffinaderier har under lång tid använt sällsynta jordartsmetaller i krackningskatalysatorer för att rena råolja (Pines 1981), något som också kan påvisas i form av ökade metallhalter i havssedimenten (Olmez m.fl. 1991). Ytterligare en föröreningsrisk utgör den ökade användningen av fosfater som gödningsmedel. Eftersom sällsynta jordartsmetaller har låg rörlighet i fosfater och oxider, vilka är stabila i miljön (Brookins 1988), kan metallerna anrikas i agrara sammanhang.

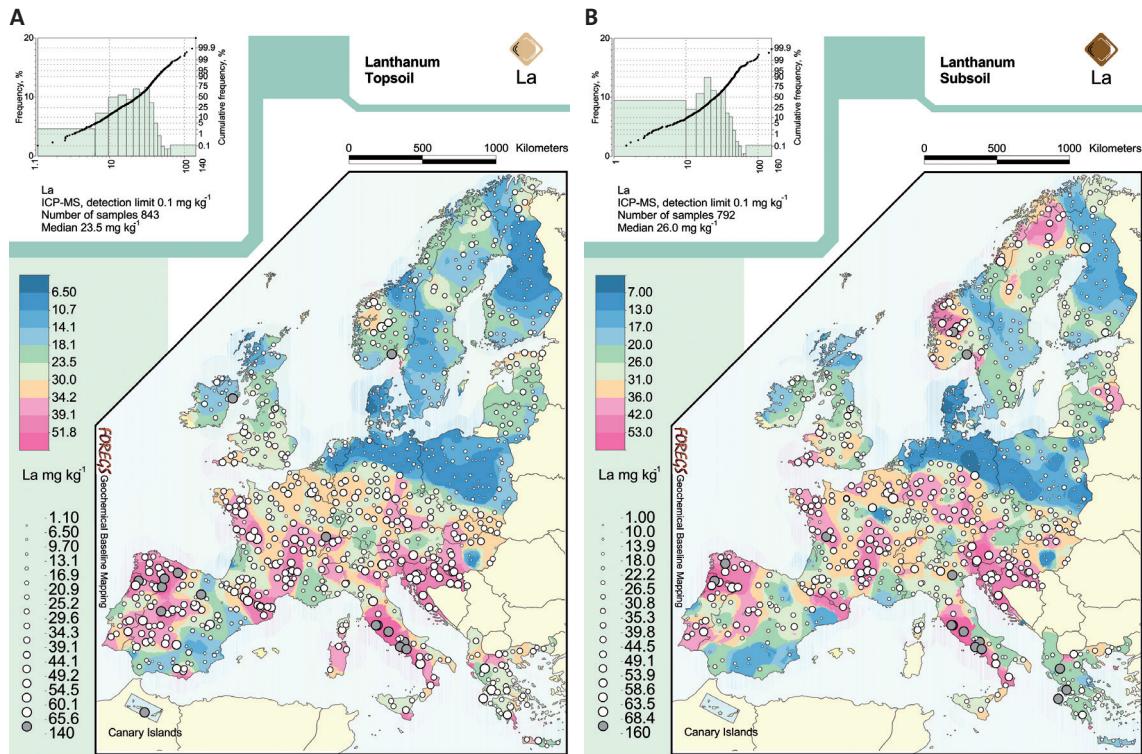
## Resultat från FOREGS databas

Kartor med beskrivningar baserade på fem olika provtagningsmedia från 26 länder har publicerats som *FOREGS Geochemical Atlas of Europe* (Salminen m.fl. 2005, se även artikel 2 och 3 i Bilaga 1). Tillgången till atlaset är fri genom webbplatsen <http://www GTK fi/publ/foregsatlas/>.

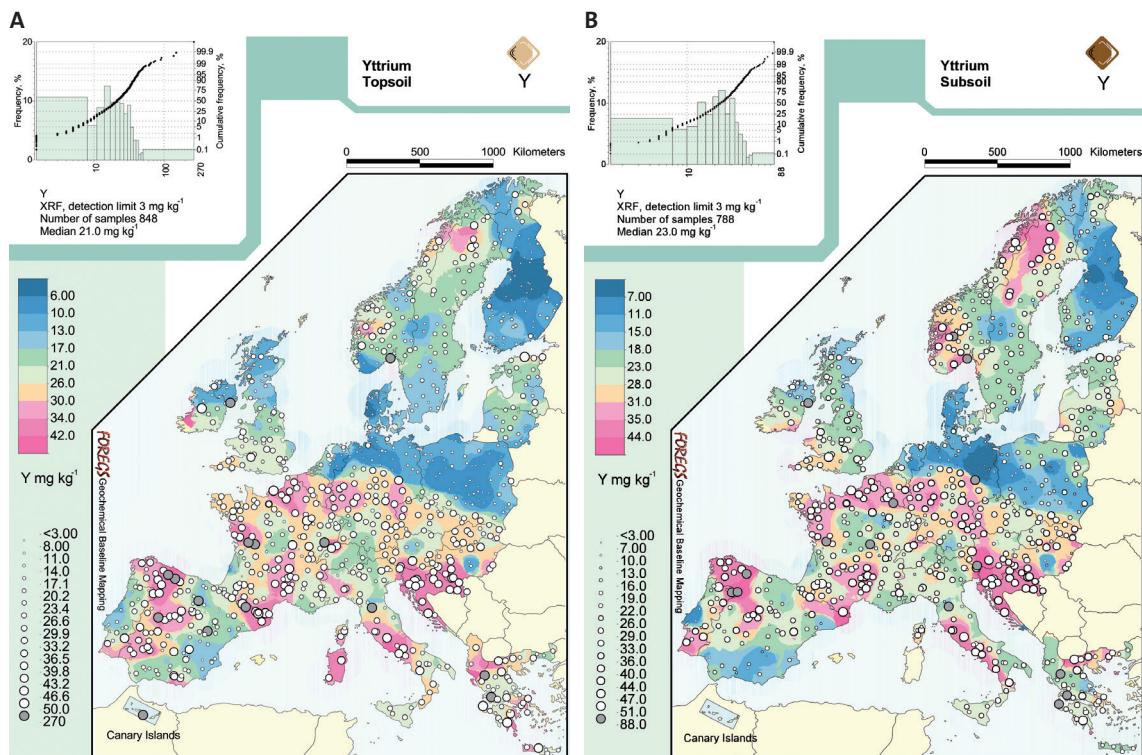
De parametrar från FOREGS vi använt i denna rapport är analysresultat av sällsynta jordartsmetaller i ytjord (topsoil) och underliggande jord (subsoil). Analyser av totalhalter med ICP-MS är utförda vid Finlands geologiska undersökning (GTK) och av yttrium med XRF på Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) i Tyskland (Sandström m.fl. 2005).

Elementkartorna från FOREGS visar spridningsmönster med areellt överdrivna anomalier vilket beror av den låga provtätheten. I Sverige baseras t.ex. kartorna på 51 prov över hela landet. På kartorna av lantan (fig. 4) och yttrium (fig. 5) i ytjord (topsoil) respektive underliggande jord (subsoil) kan man notera de betydligt lägre koncentrationerna i norra Europa jämfört med i södra Europa. Gränsen mellan områdena markeras av den senaste inlandsisens maximala läge. Skillnaden är en effekt av geologi, klimat och de lösa avlagringarnas mognad och ålder.

Statistik över medianvärdet och maximala halter av cerium, lantan och yttrium i ytjord och underliggande jord i Europa jämfört med i Sverige visar att Europa har högre median- och maxhalter än Sverige (tabell 3). Tabellen visar också att anrikningen av metallerna (kvoten mellan maximal halt och medianhalt) är betydligt högre i Europa.



Figur 4. A. Totalhalter av lantan i ytjord (topsoil, n=843). B. Totalhalter av lantan i underliggende jord (subsoil, n=792) i Europa.



Figur 5. A. Totalhalter av yttrium i ytjord (topsoil, n=848). B. Totalhalter av yttrium i underliggende jord (subsoil, n=788) i Europa.

Tabell 3. Totalhalter av cerium, lantan och yttrium i ytjord respektive underliggande jord. Medianhalter och maximala halter i Europa respektive Sverige, samt kvoten mellan dem. Observera att i statistiken för Europa ingår även det svenska analysresultatet. Europa (E), Sverige (S).

FOREGS		Fraktion	Antal (E; S)	Analysmetod	Enhet	Median		Max		Max/min	
						E	S	E	S	E	S
Ce, cerium	Subsoil	C-horizon	<2 mm	790; 51	total	ICP-MS	mg/kg	54	49	379	101
	Topsoil	0–25 cm	<2 mm	843; 51	total	ICP-MS	mg/kg	48	35	267	83
La, lantan	Subsoil	C-horizon	<2 mm	790; 51	total	ICP-MS	mg/kg	26	21	155	47
	Topsoil	0–25 cm	<2 mm	843; 51	total	ICP-MS	mg/kg	24	17	143	34
Y, yttrium	Subsoil	C-horizon	<2 mm	788; 51	total	XRF	mg/kg	23	23	88	47
	Topsoil	0–25 cm	<2 mm	845; 51	total	XRF	mg/kg	21	18	267	41

## Resultat från GEMAS databas

Kartor med beskrivningar baserade på två typer av jordbruksmark från 33 länder har publicerats i två bokvolymer som *Chemistry of Europe's agricultural soils*, part A och part B, med en medföljande DVD (Reimann m.fl. 2014, se även artikel 1 i Bilaga 1).

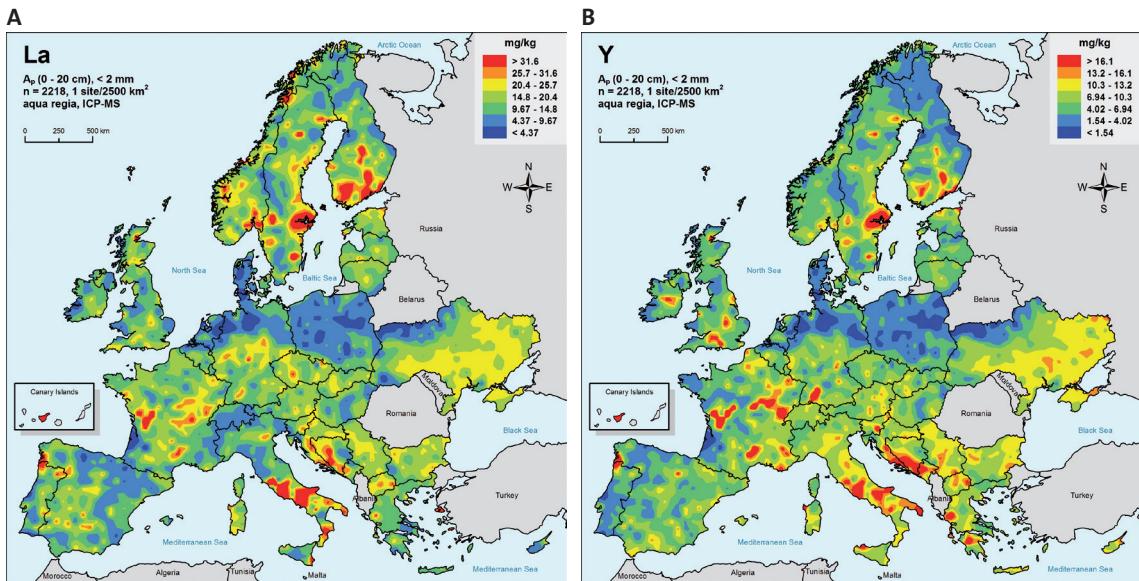
De parametrar från GEMAS vi använder i denna rapport är resultat för sällsynta jordartsmetaller och yttrium i åkermark (Ap, 0–20 cm) och betesmark (Gr, 0–10 cm) analyserade på totalhalter med XRF på BGR (Bundesanstalt für Geowissenschaften und Rohstoffe) och kungsvattenlakade halter med ICP-MS analyserat på ACME Analytical Laboratories, Vancouver. Vi har, för åkermark i Sverige, även använt analysresultat från totalhalter efter uppslutning med natriumperoxid (sodium peroxide fusion, SPF) och ICP-MS från SGS Minerals, New Jersey USA, samt en pH-neutral svag lakning med MMI-metod och ICP-MS utförd hos SGS Mineral Services, Toronto. Eftersom XRF-metoden endast levererade resultat för cerium, lantan, scandium och yttrium låt Sverige och Italien analysera totalhalterna av samtliga sällsynta jordartsmetaller med SPF-metoden, som med lägre detektionsgränser kan leverera låga halter av elementen.

Kartor över fördelningen av sällsynta jordartsmetaller i åkermark i Sverige baserade på de olika analysmetoderna finns i Bilaga 3–6.

Spredningsmönster cerium, lantan och yttrium i Europas åkermark, analyserat med XRF respektive kungsvattenlakning, visar inga generella skillnader vad gäller analysmetoden. Däremot finns skillnader i metallernas intensitet. På en europeisk skala finns inte heller någon väsentlig skillnad i distributionsmönstren vad gäller den lätta gruppen av sällsynta jordartsmetaller (fig. 6A, lantan) och den tunga gruppen (fig. 6B, yttrium).

Spredningsmönster och utbredning av anomalier för sällsynta jordartsmetaller är liknande i åkermark och betesmark. Däremot finns fler små positiva anomalier i betesmark än i åkermark. Detta förhållande kan kopplas till geologi, kemiska processer (lösighet, pH, redoxpotential) och innehåll av organiskt material, samt att jorden inte genomgått regelbunden plöjning vilket är en homogeniseringprocess som ”smeter ut” anomalierna. Positiva anomalier i åkermark som inte överlappas av anomalier i betesmark kan ha antropogent ursprung i form av användande av gödselmedel.

Medianvärden och maximala totalhalter (XRF) av cerium, lantan och yttrium i åkermark och betesmark visar att Europa har högre median- och maxhalter jämfört med Sverige. Ett undantag är lantan, där betesmark i Sverige har den högsta maxhalten i hela Europa. Tabell 4 visar också att anrikningen av metaller (kvoten mellan maximal halt och medianhalt) är högre i Europa än Sverige, men också här med undantag av lantan i betesmark. Åkermark och betesmark har relativt lika medianhalter, men för cerium och yttrium skiljer sig marktyperna något mer åt i Sverige.



Figur 6. A. Lantan (La) i åkermark (Ap) i Europa. Provtagningsdjup: 0–20 cm. Analysmetod: lakning med kungsvatten (A.R) och ICP-MS. N=2 218 (inkl. kontrollprov i analysserier). B. Yttrium (Y) i åkermark (Ap) i Europa. Provtagningsdjup: 0–20 cm. Analysmetod: lakning med kungsvatten (A.R) och ICP-MS. N=2 218 (inkl. kontrollprov i analysserier).

Tabell 4. Totalhalter av cerium, lantan och yttrium i åkermark (Ap) respektive betesmark (Gr). Medianhalter och maximala halter i Europa respektive Sverige, samt kvoten mellan dem. I statistiken för Europa ingår även det svenska analysresultatet. Europa (E), Sverige (S).

GEMAS	Marktyp	Djup	Fraktion	Antal (E; S)	Analysmetod	Enhet	Median		Max		Max/min		
							E	S	E	S	E	S	
Ce, cerium	Ap	0–20 cm	<2 mm	2108; 174	total	XRF	mg/kg	58	52	317	160	5	3
		0–10 cm	<2 mm	2023; 179			mg/kg	56	46	315	138	6	3
La, lantan	Ap	0–20 cm	<2 mm	2108; 174	total	XRF	mg/kg	23	20	155	78	7	4
		0–10 cm	<2 mm	2023; 179			mg/kg	24	20	269	269	11	13
Y, yttrium	Ap	0–20 cm	<2 mm	2108; 174	total	XRF	mg/kg	27	27	111	68	4	3
		0–10 cm	<2 mm	2023; 179			mg/kg	25	22	118	110	5	5

Jämförelse av olika analysmetoder (tabell 5) visar att medianerna för totalhalter (XRF) av cerium och lantan är dubbelt så höga som medianhalterna vid partiell lakning (A.R.) och för yttrium är de fyra gånger högre. Medianhalterna för totalhalter och kungsvattenlakade (A.R.) halter i Sverige skiljer sig endast något från Europas medianhalter. Däremot finns en påtaglig skillnad för metallerna efter extraktion med MMI®, och Sverige har betydligt högre medianhalter av cerium, lantan och yttrium än resten av Europa.

Lantan och yttrium har ungefär lika medianvärden vad gäller totalhalterna (XRF) medan medianen är betydligt lägre för de lösliga komponenterna av yttrium än motsvarande för lantan. Förklaringen är att en stor del yttrium finns i mineral som är svårlösliga, medan lantan återfinns i flera bergartsbildande och mer lättlösliga mineral.

Den procentuella lakbarheten ( $100 \times$  halt A.R./XRF) i Europa är högst för lantan (ca 60 %) medan 48 % cerium och ca 25 % yttrium generellt blir tillgängligt vid partiell lakning. De svenska proverna har betydligt högre lakbarhet vad gäller lantan (Ap: 80 %, Gr: 65 %), speciellt

Tabell 5. Cerium, lantan och yttrium i åkermark (Ap) analyserat med XRF, och lakningar med kungsvatten och ICP-MS respektive med MMI®-metoden. Betesmark (Gr) är analyserat med XRF och kungsvattenlakning och ICP-MS. Medianhalter i Europa respektive Sverige. I statistiken för Europa ingår även det svenska analysresultatet. Europa (E), Sverige (S).

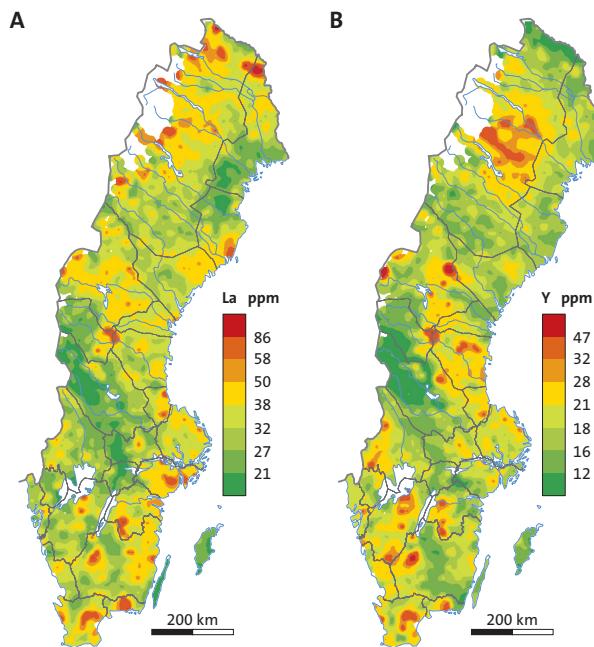
GEMAS	Marktyp	Djup	Fraktion	Antal (E; S)	Analysmetod	Enhet	Median	
							E	S
Ce	Ap	0–20 cm	<2 mm	2108; 174	A.R.	mg/kg	28	31
Ce	Gr	0–10 cm	<2 mm	2023; 179	A.R.	mg/kg	27	25
Ce	Ap	0–20 cm	<2 mm	2108; 174	XRF	mg/kg	58	52
Ce	Gr	0–10 cm	<2 mm	2023; 179	XRF	mg/kg	56	46
Ce	Ap	0–20 cm	<2 mm	2108; 174	MMI®	mg/kg	0,14	0,31
La	Ap	0–20 cm	<2 mm	2108; 174	A.R.	mg/kg	14	16
La	Gr	0–10 cm	<2 mm	2023; 179	A.R.	mg/kg	14	13
La	Ap	0–20 cm	<2 mm	2108; 174	XRF	mg/kg	23	20
La	Gr	0–10 cm	<2 mm	2023; 179	XRF	mg/kg	24	20
La	Ap	0–20 cm	<2 mm	2108; 174	MMI®	mg/kg	0,05	0,14
Y	Ap	0–20 cm	<2 mm	2108; 174	A.R.	mg/kg	6,6	6,4
Y	Gr	0–10 cm	<2 mm	2023; 179	A.R.	mg/kg	6,4	5,4
Y	Ap	0–20 cm	<2 mm	2108; 174	XRF	mg/kg	27	27
Y	Gr	0–10 cm	<2 mm	2023; 179	XRF	mg/kg	25	22
Y	Ap	0–20 cm	<2 mm	2108; 174	MMI®	mg/kg	0,18	0,39

åkermarkens prov, och cerium (60 % Ap, 54 % Gr), medan lakbarheten för yttrium inte skiljer sig från Europa. Generellt är lakbarheten högre för den lätta gruppens element (LREE) som alltså förekommer i mineral med högre vittringsbegägenhet än de mer resistenta mineral där yttrium vanligtvis ingår.

### Resultat från Geokemisk atlas över Sverige, morän

Kartor med beskrivningar av sällsynta jordartsmetaller, skandium och yttrium, baserat på morän i Sverige, har publicerats som ett avsnitt i boken *Geokemisk atlas över Sverige* (Andersson m.fl. 2014). De parametrar från atlasen vi använder i denna rapport är resultat för sällsynta jordartsmetaller och yttrium i morän <0,063 mm, analyserade på kungsvattenlakade halter med ICP-MS på ALS Scandinavia AB i Luleå. Moränproven togs på ett djup av ca 75 cm, där de är så gott som opåverkade av recent vittring.

Kartor över spridningsmönstren av sällsynta jordartsmetaller i Sverige visar hur dominansen i moränens sammansättning varierar mellan sällsynta jordartsmetaller i den lätta gruppen (LREE) och den tunga gruppen (HREE). Spridningsmönstren över landet ändrar gradvis utseende från lättaste sällsynta jordartsmetaller (La) till tyngsta sällsynta jordartsmetaller (Lu) beroende på att de sällsynta jordartsmallerna ofta ingår i samma mineral men varierar i koncentration. Anomalier av LREE i den nordligaste delen av Sverige avspeglar t.ex. arkeiska metamorfa bergarter, vilka inte framträder i spridningsmönstren över HREE. Distinkta anomalier för den tunga gruppen finns i centrala Lappland där de är kopplade till granitoider, alkalina bergarter, pegmatiter och sura metavulkaniter. HREE domineras även i sydvästra Sverige, medan LREE ger kraftigare anomalier i sydost. Kartorna nedan över lantan (fig. 7A) och yttrium (fig. 7B) representerar de båda grupperna. Övriga kartor presenteras i Bilaga 7. Flera anomalier, även svaga, av sällsynta jordartsmetaller i morän kan också kopplas till de tidigare nämnda mineraliseringstyperna för sällsynta jordartsmetaller.



**Figur 7.** **A.** Lantan (La) i kungsvattenlakad morän <0,063 mm analyserad med ICP-MS. N=2 578.  
**B.** Yttrium (Y) i kungsvattenlakad morän <0,063 mm analyserad med ICP-MS. N=2 578.

**Tabell 6.** Medianhalter, maximala halter och anrikningskvot av sällsynta jordartsmetaller, scandium och yttrium i svensk morän <0,063 mm.  
Analysmetod: kungsvattenlakning och ICP-MS. N=2 578.

Element	Undergrupp	Median (ppm)	Max (ppm)	Max/median
Ce	LREE	75	388	5
La	LREE	32	199	6
Nd	LREE	28	129	5
Pr	LREE	7,7	38	5
Sm	LREE	5,4	24	4
Sc	(LREE)	4,5	21	5
Eu	LREE	0,8	6	7
Y	(HREE)	18	163	9
Gd	HREE	4,4	22	5
Dy	HREE	3,5	23	6
Er	HREE	1,9	14	8
Yb	HREE	1,7	15	9
Ho	HREE	0,7	5	7
Tb	HREE	0,6	4	6
Tm	HREE	0,3	2	8
Lu	HREE	0,2	3	11

Medianhalterna i tabell 6 för den lätta gruppens element respektive den tunga gruppens element visar att LREE förekommer i högre koncentrationer än HREE i moränen. LREE har också högre maximala halter, men har generellt lägre anrikningskvot.

## STATISTIK ÖVER SÄLLSYNTA JORDARTSMETALLER I SVERIGE

Vi har sammanställt statistik över samtliga provmedier från Sverige i tabell 7. Anrikningskvoten i kolumnen max/median, visar hur de maximalt uppmätta värdena förhåller sig till medianhalten för respektive metall. För totalhalter av jord är de maximala halterna 2–3 gånger högre

än medianvärdet. Kungsvattenlakade halter har generellt 5–9 gånger så höga maxhalter, med undantag av lantan och yttrium från betesmark och lutetium från morän vilka har högre anrikningskvot. Lakning med MMI-metoden ger 7–24 gånger högre maxhalter än medianerna. Totalhalterna från berggrundsproven har preliminära anrikningskvoter från 9 till 35, men med osäkerhet för låga medianvärden och inte helt förutsättningslös provtagning.

Tabell 7. Faktasammanställning av sällsynta jordartsmetaller i rapportens använda provmedier. Statistiska parametrar med minimum, median och maximala elementhalter, Q25 = undre kvartil, Q75 = övre kvartil, M/M = max/median, dvs. anrikningskvot, Stdav = standardavvikelse.

Sverige	Databas	Medium	Fraktion	Analys	Metod	Antal	enhet	Min.	Q25	Median	Q75	Max	M/M	Stdav
Ce	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	0,4	24	57	89	900	16	61
Ce	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	16	60	75	96	388	5	36
Ce	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	23	43	49	67	101	2	19
Ce	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	14	24	35	47	83	2	16
Ce	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	12	42	56	73	169	3	25
Ce	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,01	0,18	0,31	0,66	3	10	0,5
Ce	GEMAS	Ap	<2 mm	A.R.	ICP-MS	174	mg/kg	6	20	31	46	141	5	22
Ce	GEMAS	Gr	<2 mm	A.R.	ICP-MS	179	mg/kg	4	18	25	40	121	5	20
Dy	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	<	0,1	2,9	4,9	38	13	3,2
Dy	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	0,9	2,9	3,5	4,3	23	6	1,4
Dy	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	2,0	3,0	3,6	4,3	7	2	1,2
Dy	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	1,5	2,3	2,9	3,4	6	2	0,9
Dy	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,6	3,6	4,3	5,2	11	3	1,5
Dy	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,004	0,042	0,071	0,133	0,479	7	0,10
Er	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	<	0,1	1,5	2,8	29	19	2,0
Er	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	0,4	1,5	1,9	2,3	14	8	0,8
Er	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	1,2	1,9	2,2	2,7	4,4	2	0,7
Er	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	1,0	1,6	1,8	2,1	4,0	2	0,6
Er	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,3	2,1	2,6	3,1	5,6	2	0,8
Er	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,002	0,029	0,046	0,086	0,545	12	0,08
Eu	SGU	Berg	mald	tot	ICP-MS	5 761	mg/kg	0,03	0,4	0,9	1,5	39		1,2
Eu	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	0,1	0,6	0,8	0,9	5,5	7	0,3
Eu	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	0,4	0,7	0,8	1,0	1,6	2	0,3
Eu	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	0,2	0,5	0,6	0,7	1,3	2	0,2
Eu	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,2	0,8	1,0	1,1	2,5	3	0,3
Eu	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,001	0,007	0,012	0,021	0,145	12	0,02
Gd	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	<	0,1	3,2	5,5	38	12	3,6
Gd	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	1,1	3,6	4,4	5,4	22	5	1,7
Gd	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	2,3	3,3	3,8	5,2	8	2	1,5
Gd	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	1,2	2,4	2,9	3,6	6	2	1,1
Gd	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,8	3,6	4,7	5,7	13	3	1,8
Gd	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,003	0,035	0,069	0,119	0,657	10	0,10
Ho	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	<	<	0,5	1,0	20		0,7
Ho	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	0,1	0,6	0,7	0,9	4,8	7	0,3
Ho	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	0,4	0,6	0,8	0,9	1,5	2	0,2
Ho	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	0,3	0,5	0,6	0,7	1,3	2	0,2
Ho	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,1	0,7	0,9	1,0	2,1	2	0,3
La	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	0	18	31	47	875	28	32
La	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	8	26	32	40	199	6	14
La	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	12	18	21	31	47	2	9
La	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	7	12	17	22	34	2	7
La	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	6	20	27	37	97	4	14
La	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,003	0,07	0,14	0,29	3,3	24	0,3
La	GEMAS	Ap	<2 mm	A.R.	ICP-MS	174	mg/kg	3	10	16	23	85	5	12
La	GEMAS	Gr	<2 mm	A.R.	ICP-MS	179	mg/kg	3	9	13	22	230	18	21

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Sverige	Databas	Medium	Fraktion	Analys	Metod	Antal	enhet	Min.	Q25	Median	Q75	Max	M/M	Stdav
Lu	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	<	0,1	0,30	0,50	9,7		0,37
Lu	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	<0,1	0,19	0,24	0,30	2,6	11	0,1
Lu	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	0,18	0,30	0,35	0,44	0,59	2	0,10
Lu	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	0,17	0,26	0,30	0,34	0,58	2	0,08
Lu	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,03	0,35	0,40	0,46	0,83	2	0,12
Nd	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	0,1	10	24	39	400	16	26
Nd	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	7	23	28	35	129	5	11
Nd	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	12	16	19	26	41	2	7
Nd	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	7	10	15	19	32	2	6
Nd	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	5	19	25	33	77	3	11
Nd	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,008	0,13	0,23	0,50	4,67	21	0,47
Pr	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	<	0,1	4,3	8,9	76	18	6,6
Pr	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	1,9	6,3	7,7	9,4	38	5	3,1
Pr	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	2,9	4,4	5,4	7,3	11	2	2,0
Pr	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	1,6	2,7	3,9	5,1	8	2	1,6
Pr	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	1,5	5,2	6,9	9,1	22	3	3,2
Pr	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,001	0,028	0,048	0,110	1,1	23	0,11
Sm	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	0,1	2,4	4,8	7,2	45	9	4,3
Sm	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	1,4	4,4	5,4	6,7	24	4	2,1
Sm	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	2,3	3,3725	3,8	5,3	8	2	1,5
Sm	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	1,4	2,125	2,8	3,725	6	2	1,1
Sm	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,9	3,8	5,0	6,3	12	2	2,1
Sm	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,002	0,031	0,061	0,113	0,86	14	0,10
Tb	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	<	0,2	0,6	1,0	97		1,67
Tb	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	0,2	0,52	0,64	0,78	3,6	6	0,2
Tb	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	0,36	0,535	0,61	0,8	1,2	2	0,21
Tb	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	0,22	0,375	0,47	0,57	1,1	2	0,18
Tb	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,1	0,6	0,7	0,9	1,9	3	0,26
Tb	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,001	0,006	0,011	0,020	0,08	7	0,01
Tm	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	<	<	0,2	0,4	46		0,69
Tm	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	0,05	0,21	0,26	0,32	2,0	8	0,12
Tm	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	0,17	0,28	0,36	0,44	0,7	2	0,11
Tm	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	0,13	0,24	0,28	0,32	0,6	2	0,08
Tm	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,03	0,34	0,41	0,47	0,9	2	0,13
Y	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	0,2	13	22	33	296	13	19
Y	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	4	15	18	23	163	9	8
Y	FOREGS	Subsoil	<2 mm	total	XRF	51	mg/kg	13	19	23	27	47	2	76
Y	FOREGS	Topsoil	<2 mm	total	XRF	51	mg/kg	9	16	18	21	41	2	6
Y	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	4	21	25	30	66	3	8
Y	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,02	0,23	0,39	0,70	3,4	9	0,62
Y	GEMAS	Ap	<2 mm	A.R.	ICP-MS	174	mg/kg	1	4	6	11	38	6	6
Y	GEMAS	Gr	<2 mm	A.R.	ICP-MS	179	mg/kg	1	4	5	9	71	13	9
Yb	SGU	Berg	mald	total	ICP-MS	5 761	mg/kg	0,1	1,3	2,2	3,5	78	35	2,5
Yb	GAOS	Morän	<0,063 mm	A.R.	ICP-MS	2 578	mg/kg	0,3	1,35	1,69	2,13	15	9	0,8
Yb	FOREGS	Subsoil	<2 mm	total	ICP-MS	51	mg/kg	1,3	1,9	2,4	3,0	4,4	2	0,7
Yb	FOREGS	Topsoil	<2 mm	total	ICP-MS	51	mg/kg	1,1	1,7	2,0	2,2	4,2	2	0,6
Yb	GEMAS	Ap	<2 mm	total	SPF	174	mg/kg	0,3	2,2	2,6	3,1	5,6	2	0,8
Yb	GEMAS	Ap	<2 mm	MMI®	ICP-MS	174	mg/kg	0,002	0,026	0,042	0,082	0,741	18	0,09

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## BILAGA 1. PUBLICERADE ARTIKLAR MED SAMMANFATTNING

### Ce, La and Y concentration in agricultural and grazing-land soils of Europe

#### *Sammanfattning av artikel 1*

Artikeln fokuserar på analyser av sällsynta jordartsmetaller i fasta provmedia, av jord från åkermark (Ap) och betesmark (Gr) insamlat inom GEMAS-projektet. GEMAS (Geochemical mapping of agricultural and grazing land soils) är ett samverkansprojekt mellan EGS (European Geological Surveys) och Eurometaux (Reimann m.fl. 2012). Analysresultaten från projektet har använts för att identifiera bakgrundsvärden för sällsynta jordartsmetaller i Sverige och Europa. I artikeln behandlas metallerna Ce, La och Y, och koncentrationerna av dessa tre element har jämförts utifrån analysmetod och markanvändning. För detta ändamål har vi använt totalhalter av sällsynta jordartsmetaller (analyserade med XRF) och elementhalter efter partiell lakning i kungsvatten (analyserade med ICP-MS). Rasterkartor över Europa har tagits fram för de tre elementen. Kartor skapades i ArcView genom interpolering med hjälp av IDW-metoden (inverse distance weighting algorithm) och klassificerades med en fractalmetod (fractal concentration area method).

Den första kartan över Europa, avseende förekomster av mineraliseringar med sällsynta jordartsmetaller och med fosfat, gjordes för att se sambandet mellan koncentrationerna av sällsynta jordartsmetaller i jord och mineraliseringar med sällsynta jordartsmetaller och fosforförekomster. I artikeln beskrivs 40, 37 och 30 anomalier av Ce, La respektive Y. Av dessa finns sju ceriumanomalier, sex lantanomalier och fem yttriumanomalier i Sverige. Artikeln introducerar också ett sätt att upptäcka nya mönster på kartorna över sällsynta jordartsmetaller med kvoterna Y/Ce och Y/La, vilka tydligt visar korrelationen mellan anomalierna och förekomsten av ophioliter och, på många platser i Europa, alkalina bergarter och karbonater.

#### *Summary of paper 1*

GEMAS data have been investigated with focus on rare earth elements (REE) in two solid media of top soil from agriculture (Ap) and grazing land (Gr) soil to identify the background value of rare earth elements in Sweden and Europe. GEMAS is a collaboration project between the EGS (European Geological Surveys) and Eurometaux (Reimann et al. 2012). In this paper, Ce, La and Y concentrations are discussed. The Ap and Gr samples were obtained by partial leaching in aqua regia and analysed by ICP-MS. Total concentrations were analysed by XRF. The concentrations of those three elements have been compared based on analytical method and sample media. The raster maps for the three elements were produced for the whole of Europe. Using ArcView software and the IDW (inverse distance weighting algorithm) method, maps were generated and then classified using the fractal concentration-area (CA) method.

The first European map of REE and phosphate –bearing mineralisations was produced to see the correlation between REE concentration in soil and the presence of REE and phosphate-bearing mineralisations. In this paper, 40, 37 and 30 anomalies of Ce, La and Y, respectively, were described. Of these, seven cerium anomalies, six lanthanum anomalies and five yttrium anomalies are located in Sweden. In this paper, ratio maps of REE are introduced as a tool for prediction of some major rocks at a continental scale. The maps clearly show that ratios of Y/Ce and Y/La correlate with occurrences of ophiolites, and also in several places in Europe represent alkaline and carbonate rocks.

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## Ce, La and Y concentrations in agricultural and grazing-land soils of Europe

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### ABSTRACT

Ce, La and Y from agricultural (Ap) and grazing land (Gr) soils of Europe have been investigated using new geochemical data produced by the GEMAS (Geochemical mapping of agricultural and grazing land soils) project. Interpolated maps showing Ce, La, and Y distributions in Ap and Gr were generated using ArcView and classified with the concentration – area (CA) fractal method. The median values of the investigated elements show similar concentrations in Ap and Gr soils, while the median values obtained by XRF-total analyses are generally higher than those obtained by aqua regia extraction, ICP-MS (aqua regia). In general, high pH alkaline soils have higher REE concentrations while specific anomalies can often be correlated with known phosphate and REE mineralizations. The GEMAS and the topsoils media from the FOREGS (Forum of European Geological Surveys) Project databases are compared. FOREGS geochemical data shows larger extended anomalies, such as the European wide north–south division, which are difficult to attribute to local processes, while the GEMAS anomalies are spatially more restricted, and can be related to a number of more local factors (e.g., climate, geology, pH, clay content and presence of till).

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### 1. Introduction

GEMAS is a collaboration project between the Geochemistry Expert Group of EuroGeoSurveys (EGS) and Eurometaux (European Association of Metals) (Reimann et al., 2012a,b). The main goal of the GEMAS project is to produce an internally consistent set of soil geochemistry data at the European scale based on REACH (EC, 2006) requirements. More information concerning the methodology, the collection and the preparation of samples can be found in Reimann et al. (2009, 2012a) and EGS (2008). REE data from the FOREGS (Geochemical baseline

mapping data base) database has previously been investigated at a national and European scale (Salminen et al., 2005a,b; Salpeteur et al., 2005; Sandström et al., 2005; Tarvainen et al., 2005). Fedele et al. (2008) investigated anthropogenic sources of REEs in Europe while Petrosino et al., 2013-this issue compared the REE concentrations in Sweden and Italy, and Sadeghi et al., 2013-this issue investigated the REE distribution compared with mineralization in Sweden.

REEs show similar chemical and physical properties and represent a geochemically coherent group (Hu et al., 2006). REEs show an affinity for oxygen and are found in concentrated form in phosphorites and in argillaceous sediments. REEs in soils generally originate from locally derived geological parent materials (Liu, 1988), however the use of fertilizers is also an important entry path for REEs into soils. The solubility of REEs in water varies based on the host mineral. The exchangeable REE content in soils also varies between trace and concentrations of up to 24 mg/kg (Hu et al., 2006). Ca-minerals, particularly igneous rock-forming minerals such as hornblende, augite, apatite, and fluorite, can bind most REEs during magmatic and hydrolysis processes (Liu, 1988). Considerable amounts of REEs in soils exist in the form of carbonates. Some researchers (e.g., Zhu and Xing, 1992) therefore suggest that carbonate-bound REEs should be classified as an independent REE form within soils. Many factors play a role in the REE concentrations in soil, e.g. adsorption and desorption processes, physical and chemical characteristics of the soils (Ran and Liu, 1993), pH (Dong et al., 2001), presence of organic material (Beckwith and Butler, 1993), and timing for establishment of an equilibrium of desorption (Li et al., 2000).

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There are several potential anthropogenic sources of REEs in the environment including acid mine drainage (Haxel et al., 2002; Protano and Riccobono, 2002), contamination from nuclear reactors and their waste streams (Brookins, 1984; Rard, 1988), and REE-doped zeolites which have been used as fluid-cracking catalysts in the petroleum industry since the 1960s (Pines, 1981) and have subsequently been detected in offshore sediments (Olmez et al., 1991). The increasing use of REEs in industrial processes suggests that REE release into the environment is likely to increase in the future with potential impacts on human health (Haley, 1991; Hirano and Suzuki, 1996). In the GEMAS project only the REEs Ce and La were analyzed, therefore, in this paper, we focus on these two elements and on Y which, while not a REE itself, follows the heavy REEs chemically and can therefore be used as an analog for those elements (McLennan, 1989).

Cerium (Ce), atomic number 58, is the lightest and the most abundant of the REEs, and forms several minerals including monazite, xenotime, bastnäsite and cerite. Cerium, generally found in the trivalent state, differs from other REEs because, under highly oxidizing conditions, it can also occur as  $\text{Ce}^{4+}$ , leading to a 15% size reduction and to a smaller solid-state ionic radius. The relationship between  $\text{Ce}^{+3}/\text{Ce}^{+4}$  is useful for understanding marine and surficial redox geochemistry. Accessory minerals such as allanite, apatite, zircon and sphene are important in the enrichment of Ce in igneous rocks. The crustal average for Ce is 60 mg/kg, with a lesser content in mafic rocks (average 30 mg/kg) than in granite, where it can reach 8230 mg/kg (Mason and Moore, 1982). The abundance of Ce in soils varies from 15.8 to 97.4 mg/kg, with a mean of 48.7 mg/kg. Kabata-Pendias (2001) mentioned that soils developed on calcareous parent rocks show a comparative enrichment in REEs.

Lanthanum (La), atomic number of 57, usually occurs with an oxidation state of +3. It is the largest of the trivalent REEs. Lanthanum is a lithophile element under most conditions and forms several minerals, including monazite, which is relatively common, and cerite; it is also widely dispersed in trace quantities in most rocks and minerals (e.g., biotite, apatite, pyroxene and feldspar). Lanthanum levels in igneous rocks vary depending on the rock type (e.g. basalt up to 15 mg/kg, granite 45–55 mg/kg, giving an average crustal abundant of 37 mg/kg). The behavior of La during metamorphism is not well understood, however partial melting is known to contribute to La enrichment in the lighter minerals/leucosome during migmatization. High La values are generally found in felsic rocks, especially intrusives, and in the soils derived from them. In soils derived from sedimentary rocks, La concentration closely corresponds to that of the parental rock, with the exception of limestones, where the soil is enriched with respect to the parent rocks (Wedepohl, 1995).

Yttrium (Y) belongs to the group 3 of the periodic table, which also includes Sc, Lanthanides and Actinides. The element has an atomic number of 39 and occurs with an oxidation state of +3. Under most conditions Y is lithophile. Chemically, it resembles the heavier REEs. The major importance of Y in geochemistry is that it has a geochemical behavior intermediate between that of the smaller REE lanthanide elements dysprosium (Dy) and holmium (Ho) (McLennan, 1989) and therefore provides a good proxy for the heavy REEs. It is strongly partitioned into garnet, hornblende, clinopyroxene and biotite, but also shows a slight enrichment in granitic rocks (ca. 40 mg/kg) relative to intermediate (ca. 35 mg/kg) and basaltic (ca. 32 mg/kg) igneous rocks. Yttrium concentration in basalt is sensitive to the degree of partial melting involved in the formation of the magma (Wedepohl, 1978, 1995). Low Y concentrations may occur in calc-alkaline magmas as a result of the stabilization of phases rich in heavy REEs in the source region, and/or of their removal from the magmas during fractional crystallization. Elevated Y values are generally found in felsic rocks, especially intrusive, and in the soils and stream sediments derived from them. There is little information about the behavior of Y in the soils (Kabata-Pendias, 2001) but the average value of Y concentration is 23 mg/kg and 15 mg/kg in uncultivated and cultivated soils, respectively.

The main aim of this paper is to illustrate the distribution of La, Ce and Y in European agricultural (Ap) and grazing (Gr) soils, using the GEMAS database, to identify patterns that can be related to bedrock geology and mineralisation, and to compare our results with those obtained on topsoils medias by the FOREGS European Project.

## 2. REE mineralizations in Europe

A number of maps and papers covering different themes within the study area of the GEMAS project (e.g., geology, structure and fracture zones, distribution of different rock types, topography, and distribution of main sedimentary basin and soil of Europe) can be found in Reimann and Birke (2010), Asch (2003) and Jones et al. (2005).

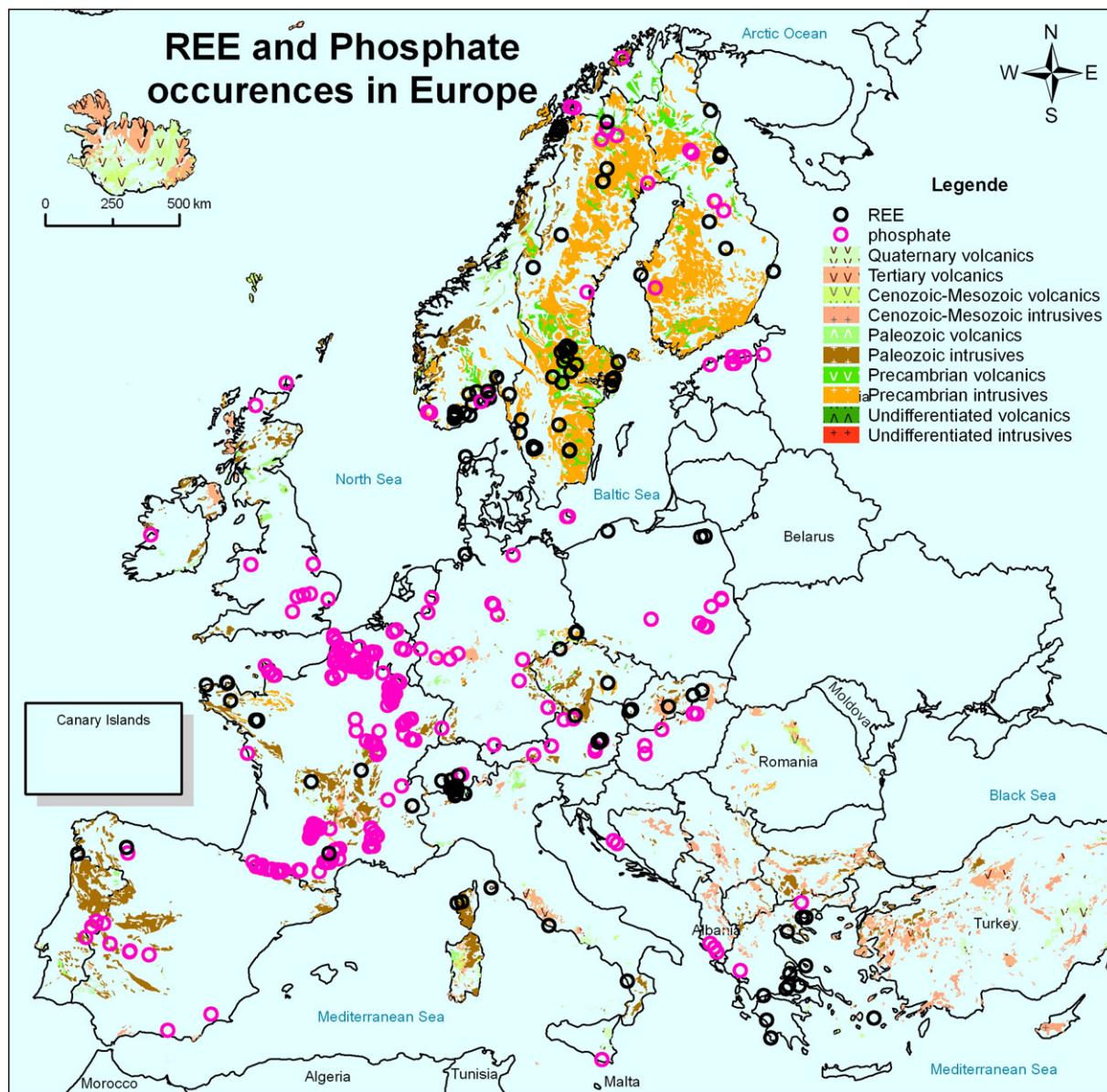
Since 2003, the Geological Surveys of Finland, Norway, Russia and Sweden have carried out a joint project on the metallogeny of Fennoscandia (FODD project) (Eilu, 2011) compiling significant information gathered from mining and exploration company reports. In 2009 the ProMine project started. This project has been the European commission's principal project in the field of exploration and efficient use of mineral resources within Europe. The project has been carried out by 30 partners from 11 EU countries. The mineral resources map for the whole of Europe is downloadable from the ProMine portal (Promine gtk.fi). All mineralizations from the ProMine and FODD databases where REEs and phosphates are the main commodities were extracted. Fig. 1 shows the distribution of volcanic and plutonic rocks of Europe extracted from IUGS digital map (Pawlewicz et al., 2002) and the location of known REE and phosphate ore deposits within GEMAS project study.

Visually there is a very good spatial association between anomalies based on GEMAS interpolated maps and distribution of granitoids/felsic alkalic volcanic rocks. In general the interpolated maps from GEMAS data (e.g. in Scandinavia, Italy, Spain, UK etc.) show good spatial association between REEs distribution and phosphate mineralization.

## 3. Results and discussion

### 3.1. Distribution of Ce, La and Y in Europe

Elemental concentrations in Ap and Gr media were obtained by partial leaching of sample in aqua regia followed by analysis of the leachate by ICP-MS (hereafter denoted aqua regia), and by whole sample analysis by XRF (denoted XRF-total). Basic statistical parameters for La, Ce and Y are presented in Table 1. Figs. 2–4 show interpolated geochemical maps produced with Arcview GIS software using the inverse distance weighted (IDW) algorithm to generate a regular grid with a  $6 \times 6$  km cell size and a circular window with fixed radius of 150 km. Color intervals were assigned using the fractal CA model (fractal concentration-area model) available in GeoDAS (Cheng et al., 2001) in order to avoid excessive data smoothing and preserve the original data distribution (Lima et al., 2003, 2008). Since the distribution patterns of La, Ce and Y for Ap and Gr European soils are quite similar, only maps for Ap soils analyzed by aqua regia (Table 1) are given (Figs. 2–4). Of particular note, the spatial distribution of Ce, La and Y between northern and southern Europe are significantly different, reflecting both geological and climate variations. In the northern part of Europe, north from the last glacial maximum, Ce, La, and Y concentrations are generally low except for on the Scandinavia peninsula. In the latter area the distribution of high Ce, La and Y concentrations reflects either exposed crystalline rocks (e.g., in northern Sweden) or marine, clay rich sediments (e.g., in central Sweden and southern Finland). As shown in Fig. 5, in Norway, Sweden and Finland, Ap soils tend to display higher median values of Ce, La, and Y than Gr soils. This is thought to be related to differences in pH between none plowed grassland (lower pH) and arable soils (more alkaline pH). All REEs are more concentrated in alkaline than in acid soils, hence soils developed on calcareous rocks have a comparative enrichment of REEs,



**Fig 1.** Distribution of main rock types of volcanic and plutonic formations together with known rare earth elements (REEs) and phosphate mineralization within GEMAS project study area.

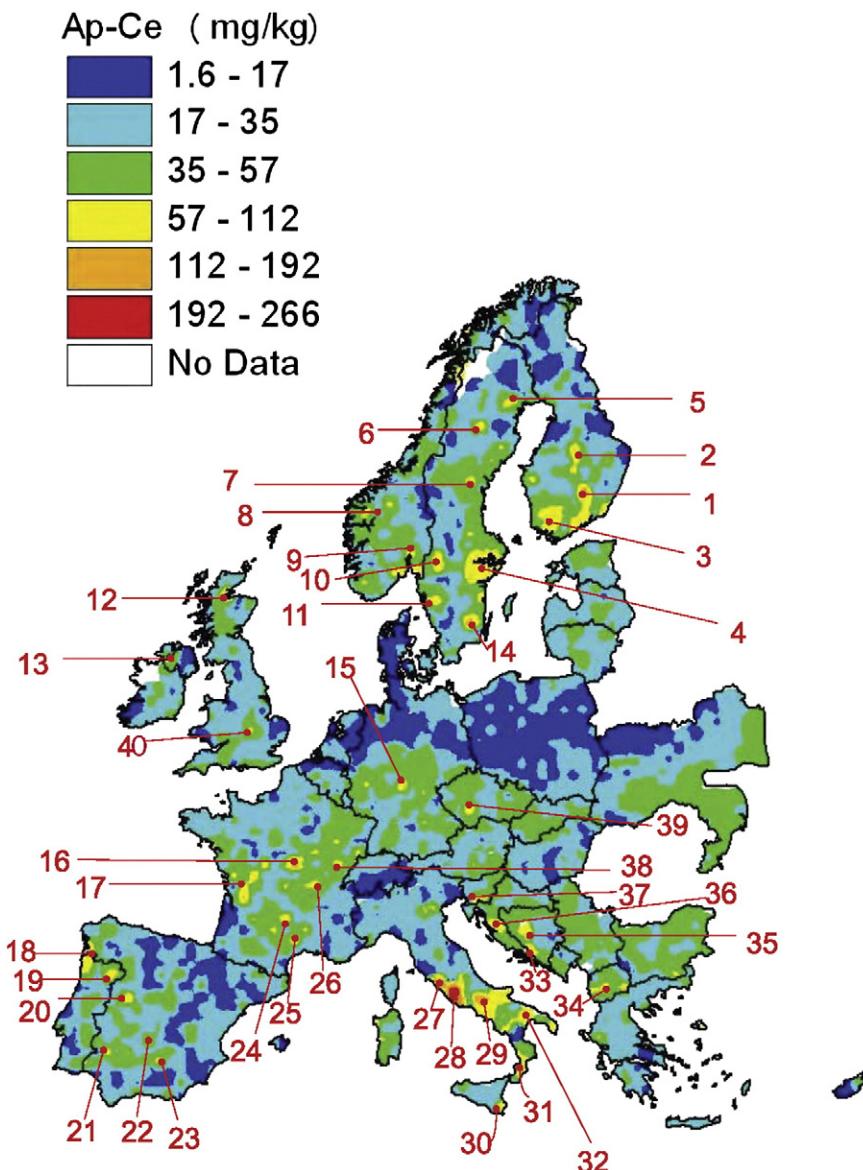
thought to be due to the removal of the hydroxide complexes in acid environment (Kabata-Pendias, 2001). An alternative explanation for these anomalies is the excessive use of phosphates in agricultural practices.

Indeed, Ce, La and Y have low elemental mobility in phosphates and oxides that are very stable in the surface environment (Brookins, 1988). An opposite pattern occurs in Estonia, where the grazing land samples

**Table 1**

Summary statistics, major elements, agricultural soil (Ap-samples, 0–20 cm, b2 mm fraction, N = 2108) and grazing land soil (Gr samples, 0–10 cm, b2 mm, N = 2024). All analytical results are in mg/kg. Analysis of REE after aqua regia assays by ICP-MS and XRF-total (Total), LDL: Lower detection limit.

REEs	Material	LDL	Analytical method	Median	Minimum	Maximum	Lower quartile	Upper quartile	Std. dev.	Standard error
La	Ap	0.1	Aqua regia	14.3	1.0	109	9.4	19.9	10.0	0.21
La	Ap	20	XRF-total	23	10	155	10	32	15.1	0.33
La	Gr	0.1	Aqua regia	13.6	0.9	229	8.9	19.0	11.5	0.25
La	Gr	20	XRF-total	24	10	269	10	34	16.8	0.37
Ce	Ap	0.1	Aqua regia	28.3	1.6	265	18.5	39.4	19.7	0.43
Ce	Ap	20	XRF-total	58	10	317	40.5	75	28.7	0.62
Ce	Gr	0.1	Aqua regia	27.1	1.6	272	17.5	37.8	19.1	0.42
Ce	Gr	20	XRF-total	56	10	315	37	73	28.5	0.63
Y	Ap	0.01	Aqua regia	6.6	0.2	64	3.9	9.9	5.5	0.12
Y	Ap	3	XRF-total	27	6	111	20	33	10.1	0.22
Y	Gr	0.01	Aqua regia	6.4	0.2	76	3.8	9.7	6.7	0.14
Y	Gr	3	XRF-total	25	3	118	18	31	11.0	0.25

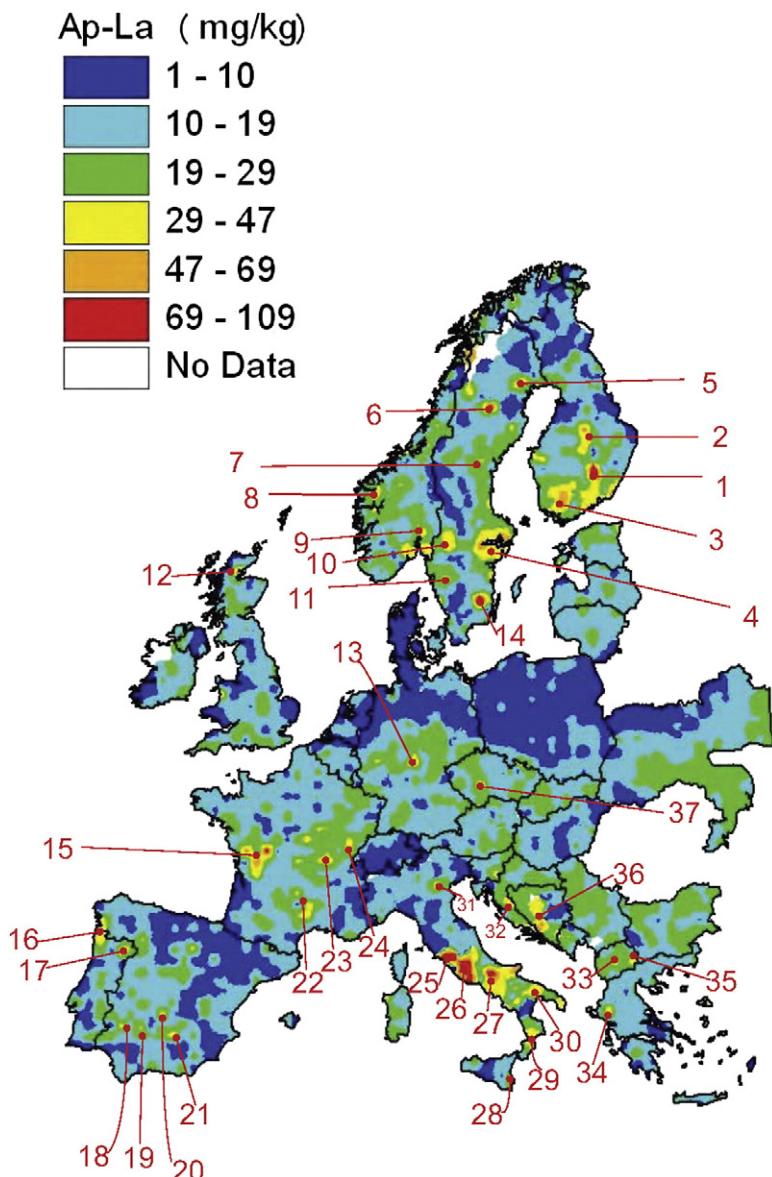


**Fig 2.** Numbered cerium interpolated maps for agricultural soil (AP) (in mg/kg) (see Table 2 for more explanation of numbered anomalies).

overlying Paleozoic black shale enriched in Ce, La, and Y, have concentrations of these elements higher than agricultural soils. In general, the median values of Ce, La and Y concentrations in both Ap and Gr soils are higher in Balkan and Mediterranean countries, testifying to the strong influence of the warm climate on the secondary concentration of La, Ce and Y in soils. In southern Europe and the Mediterranean region, climate and erosion style also play an important role. Many areas with paleosols and residual soils (*terra rossa*, developed on limestone) show high La, Ce and Y concentrations. In these regions (e.g., Italy, Greece, Cyprus, Portugal, Hungary, Croatia), high REE concentrations occur in grazing land samples where clay-rich layers with iron oxides developed within the soil horizon and have not been reworked by plowing.

Summarizing, the maximum concentrations of studied elements occur in northern Europe (Norway, Sweden, Finland), as well as in France, Italy, Spain and UK and, to a lesser extent, in Greece, the Czech Republic and Estonia. Maximum values tend to be higher in grazing land samples than in agricultural soils (especially for Y). There are however exceptions where the Ap soils are more enriched than Gr soils, e.g., La in Norway, Greece, France; Ce in France, Sweden, UK, Finland; Y in Spain.

**Cerium (Ce):** The highest values of Ce in European Ap and Gr soils are 265.05 mg/kg and 272.37 mg/kg, respectively. The median values of Ce contents are 28.37 mg/kg and 27.14 mg/kg in Ap and Gr soils, respectively, analyzed by aqua regia, compared with 58 mg/kg and 56 mg/kg in Ap and Gr, respectively, by total. Fig. 2 shows the Ce distribution pattern and high concentration areas are numbered with explanations presented in Table 2. Box plots (Fig. 5a) compare Ce concentrations in Ap and Gr soils, in the European countries. The Ce in Ap has high values over southern part of Finland and central part of Sweden, thought to be due to high concentrations of clay minerals in soils as well as underlying greywacke, sandstone schist and, particularly in Sweden, to skarn sulfide mineralization. In the northern Sweden, Ce anomalies in Ap are thought to be due to underlying Paleoproterozoic intrusive rocks (granite-quartz monzonites with some minor anallite mineralization). High Ce concentrations in central and southern Sweden correlate with evolved granites. The Ce anomalies in northern Sweden can be related to Fe mineralizations, e.g., Kiruna type apatite-Fe deposits. Along the Caledonian orogenic front in Scandinavia some of the anomalies are thought to be due to underlying younger granite, and in Sweden are also associated with skarn mineralization (e.g., the Soliden W-Fe mineralization).



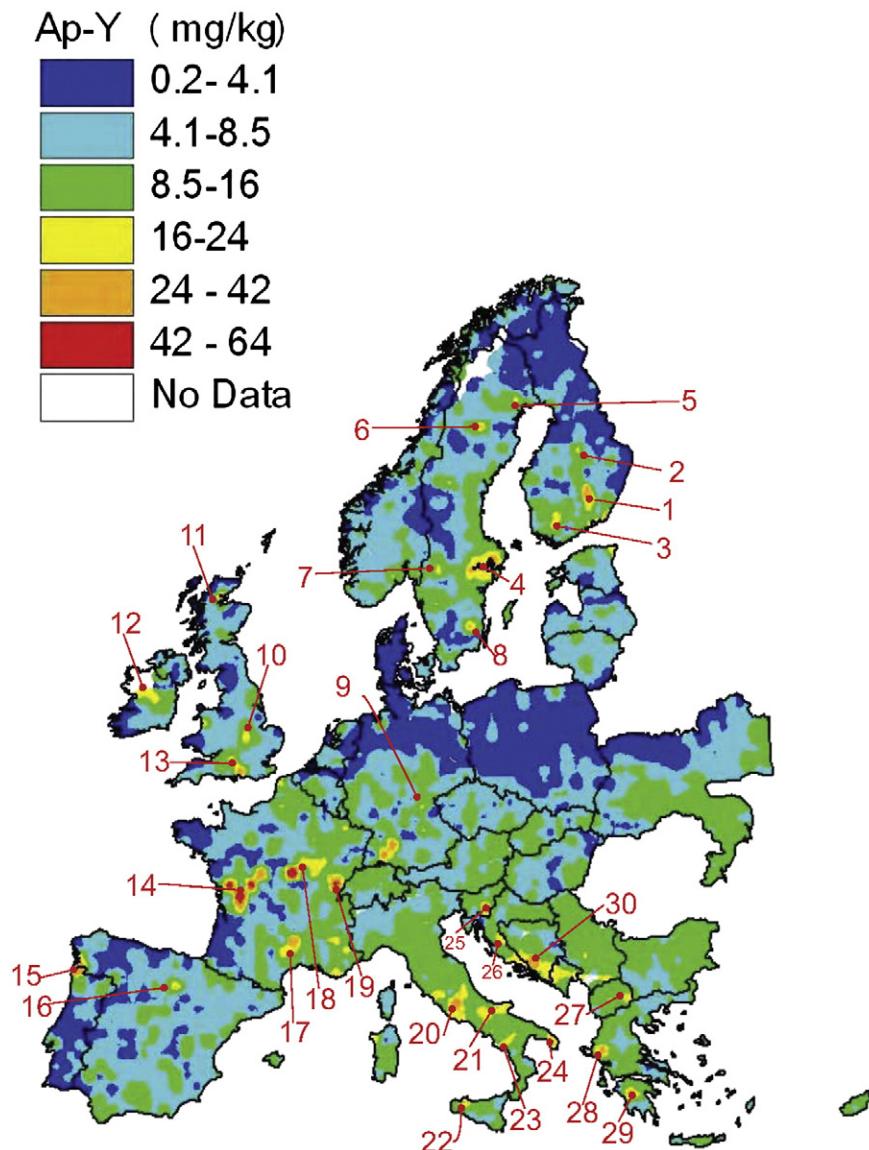
**Fig. 3.** Numbered lanthanum interpolated maps for agricultural soil (AP) (in mg/kg) (see Table 3 for more explanation of numbered anomalies).

Cerium anomalies occur associated with: Precambrian and Paleozoic schists and gneisses in Macedonia; Variscan granitic and metamorphic rocks in northern Portugal and western Spain; Cretaceous phosphates and, in some cases, Silesian coal in central France; Permian volcanic rocks and Lower-middle Jurassic rocks in southern France; carbonate rocks and bauxite mineralizations in Bosnia and Herzegovina; high potassic plutonic rocks (in many cases in strong correlation with K, Th, U, Cs and Mg) in Czech Republic; Tertiary volcanic rocks in Germany; and finally, the alkaline volcanic province (where the greatest anomalies occur) in central-southern Italy and igneous and metamorphic pre-Alpine basement in Calabria, southern Italy. However, Ce anomalies in the Pachino area (Sicily), in particular, may be related to intensive agricultural activities.

Lanthanum (La): Aqua regia data for La concentrations in Europe give a median of 14.3 mg/kg and 13.6 mg/kg with maximum values of 109.3 mg/kg and 229.6 mg/kg in Ap and Gr soils, respectively. By comparison, total analysis of La returns a median value of 23 mg/kg and 24 mg/kg and maximum value of 155 mg/kg and 269 mg/kg in Ap and Gr, respectively. Fig. 3 shows La distribution pattern with high concentration areas numbered. Table 3 reports the explanation for each numbered area. Box plots reported in Fig. 5b compare La

concentrations in Ap and Gr soils, in the European countries. The La Ap soils map shows that several anomalies are very similar to the Ce anomalies. The anomalies are associated with: peat soils, clay minerals and granitic-migmatitic rocks in Finland; leucogranites, pegmatites, clay-rich soils (secondary La concentrations), migmatized bedrock with well-developed leucosome in Sweden (Sadeghi et al., 2013-this issue); Precambrian and Paleozoic schist and granitic rocks in Macedonia; granitic rocks in northern Portugal and western Spain; Tertiary-Quaternary cover with high concentration of Fe and silicified coal, Permian volcanic and Lower-middle Jurassic rocks in France; carbonate rocks and bauxite mineralization in Bosnia and Herzegovina; granitic rocks in Czech Republic, and Tertiary volcanic rocks in Germany; phosphorite, lignite and/or the Pliocene sediments with material derived from the limestone and phosphorite in Greece; volcanic products of the alkaline province in Italy. However some local anomalies may be related to anthropogenic sources in areas where steel industries and intense agricultural activities are present.

Yttrium (Y): The highest values of Y in European soils are 64.5 mg/kg and 111 mg/kg, with the median values of 6.6 mg/kg and 6.4 mg/kg in Ap and Gr samples, respectively, analyzed by aqua regia method. Those contents result median values of 27 mg/kg and 25 mg/kg in Ap



**Fig 4.** Numbered yttrium interpolated maps for agricultural soil (AP) (in mg/kg) (see Table 4 for more explanation of numbered anomalies).

and Gr soils, respectively, when analyzed by total method. Fig. 5c shows the Y distribution pattern and high concentration areas numbered. Table 4 reports explanations for each numbered area. Box plots reported in Fig. 5c compare Y concentrations in Ap and Gr soils in the European countries. The distribution of Y anomalies shows slight differences compared to the Ce and La anomalies due to the geochemical behavior of Y, similar to HREEs, as opposed to the LREEs. High values in Ap and Gr soils are associated with: crystalline basement of the Iberian Massif in northern Portugal and Spain, as well as in the Scandinavian countries and Italy; the alkaline volcanic/magmatic provinces in Italy and northern Greece; granitic basement with high U content in Bosnia and Herzegovina; residual soils on karst and red soils in Croatia; phosphorite, lignite and sediments with material derived from the phosphorite, and residual soil developed on limestone in Greece; acid volcanic rocks (volcanogenic sediments) in a Permian basin (Stockeimer) in Germany; black marls and Silesian coal, in France; clay mineral, greywacke and/or sulfide mineralization and granitic-migmatitic rocks in Scandinavia; Fe mineralization, (e.g., Kiruna) and skarn mineralization (e.g., Soliden W-Fe mineralization) in Sweden; alkaline volcanic rocks and possibly bauxite deposits in Apulia (e.g., Alta Murgia, Otranto area) in Italy.

### 3.2. Comparing the Ap and Gr sample media

The median concentrations of La, Ce and Y in Ap and Gr samples obtained by the two analytical methods used (aqua regia MS and total) are similar. The median values for total method are almost two times higher for La and Ce (extractability of ca 60% and 50%, respectively) and 4 times higher for Y (extractability of ca 25%). Extractability among the three elements is the highest for La (ca 60%), whereas almost 50% of Ce and 25% of Y can be leached from the sample by the aqua regia method.

Lanthanum shows much higher maximum concentrations in Gr than in Ap samples (230 mg/kg versus 109 mg/kg for aqua regia method and 269 mg/kg versus 155 mg/kg for total method, respectively). For Ce and Y maximum concentrations for both Ap and Gr are similar with difference up to 3% for Ce (aqua regia) and 16% for Y (aqua regia). The main difference between elemental distribution of La, Ce and Y is related to the geochemical behavior of the single investigated element, its extractability and its source.

The standard deviation showing the spread of concentrations in Ap and Gr samples is similar for both soil types. Cerium shows the highest concentrations and median values with the largest spread of

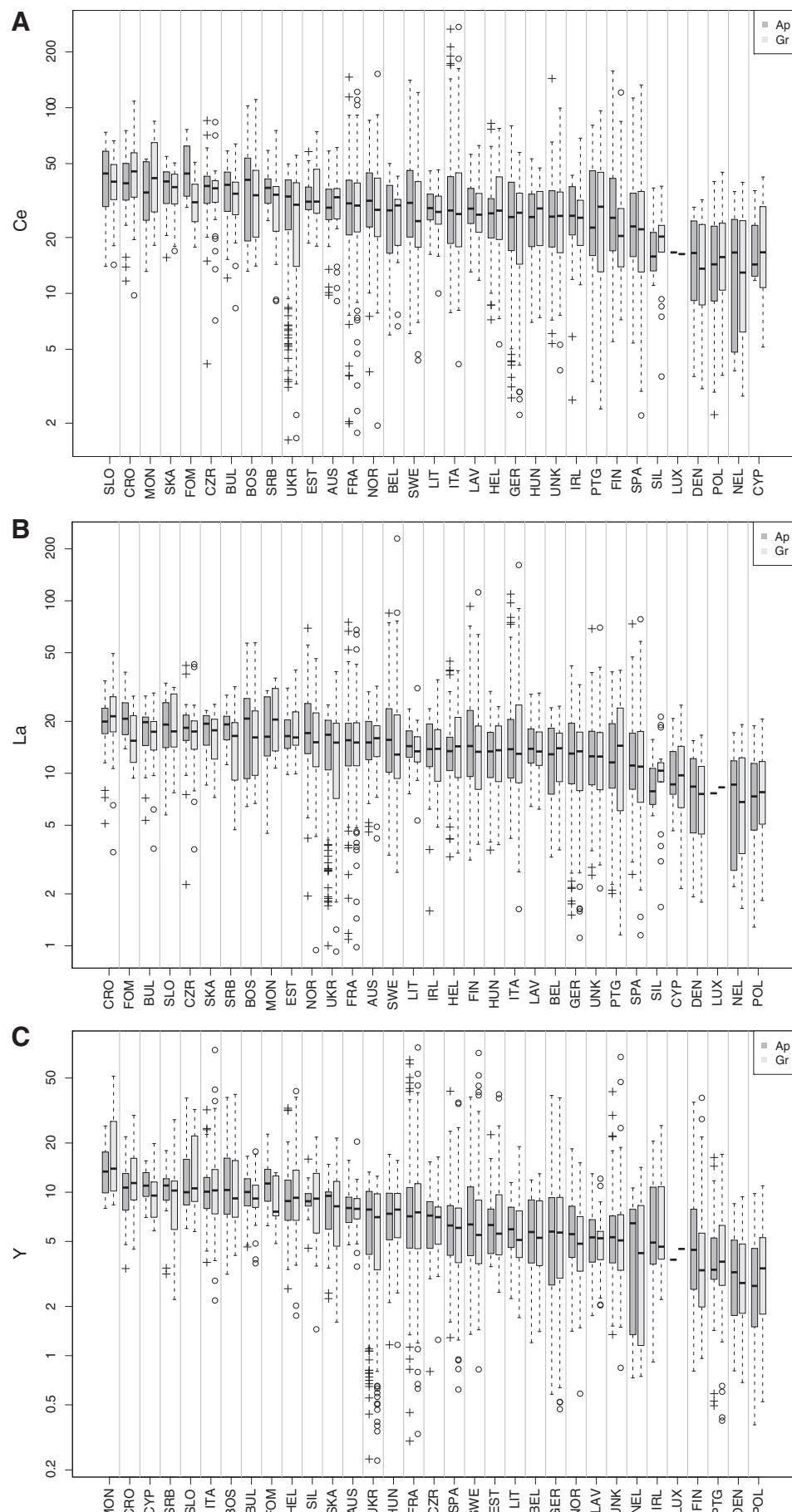


Fig 5. Box plot comparison of Ap and Gr in respective countries. a) Ce, b) La, and c) Y.

**Table 2**

Explanation of the numbered cerium anomalies in the interpolated maps for agricultural soil (AP) (in mg/kg) analyzed by ICP-MS.

Ce anomalies (Ap)	Country	Explanation of the anomalous values
1	Finland	Peat soils, varying bedrock
2	Finland	Clay soils, association with large anomaly in regional till geochemistry, metasedimentary or granitic rocks
3	Finland	Clay soils with granite–pegmatite–magmatic bedrock
4	Sweden	Clay minerals, graywacke, sandstones, schist. Sulfide mineralization in Bergslagen, e.g., Jadersbruk sulfide W, Pb, Zn, Cu, Ag and calc-silicate skarn
5	Sweden	Granite–pegmatite–migmatite bedrock
6	Sweden	Paleoproterozoic intrusive rocks (granite–quartz monzoite association with some small anallite mineralization)
7	Sweden	Carbonatite and nepheline syenite in the Alnö Area
8	Norway	Sveconorwegian granitoid, granite, pegmatite
9	Norway	Sveconorwegian granitoid, granite, pegmatite
10	Sweden	Younger granite of Sveconorwegian age and Soliden W–Fe skarn mineralization
11	Sweden	Younger granite–pegmatite in Sveconorwegian orogen
12	UK	Faeroes–Shetland–Orkney basin, Paleozoic–Precambrian metamorphic rocks
13	UK–Ireland	Paleozoic–Precambrian metamorphic rocks, Ireland–Scotland platform,
14	Sweden	W mineralization in skarn and granite bedrock
15	Germany	Tertiary (Oligocene–Miocene) volcanics of Kuppenrhön (Wasserkuppe near Abtsroda),
16	France	Cretaceous phosphate and Eocene paleosoil
17	France	Alteredites over J1–J2 Formation.
18	Portugal	Paleozoic intrusive rocks of the Iberian Massif
19	Portugal	Paleozoic volcanic rocks of the Iberian Massif
20	Spain	Paleozoic–Precambrian metamorphic rocks of the Iberian Massif,
21	Spain	Paleozoic intrusive–metamorphic rocks of the Iberian Massif.
22	Spain	Paleozoic intrusive rocks and some Jurasic–Neogene volcanic rocks belonging to Alentejo–Guadalquivir Basin in the Iberian Massif
23	Spain	Silurian–Ordovician rocks of Iberian Massif
24	France	Black marls, Lower–Middle Jurassic, enriched in LREE
25	France	J1–J2 and Permian volcanics
26	France	Silesian coal
27	Italy	Southern Tuscany alkaline volcanic area
28	Italy	Latiun alkaline volcanics
29	Italy	Roccamontina alkaline volcanics
30	Italy	Anthropogenic source. In the area occur oil refineries (Vittoria) and there is intense agricultural activity (Pachino).
31	Italy	Igneous and metamorphic pre-Alpine basement
32	Italy	Anthropogenic source. It corresponds with the Taranto area, where steel factories and intense agricultural activity as well is present
33	Bosnia & Herzegovina	The soils cover carbonate rocks; Terra Rossa residual soils. Deposits of bauxite
34	Macedonia	Precambrian and Paleozoic schists and Precambrian gneisses
35	Bosnia & Herzegovina	Permotriassic sandstones with quartz veins. Au and Fe deposits
36	Croatia	Residual red soil – Terra Rossa
37	Slovenia	Carboniferous sediments
38	France	Paleocene Bresse graben (alterite?)
39	Czech Republic	High-potassic (high K–Mg) plutonites–Durbachite (Certovo bremeno suite). These rocks contain elevated concentrations of the LIL elements K, Th, U, Rb, Cs, Ba (often > 2000 ppm), Sr (often > 1000 ppm) in combination with relatively high content of MgO (mostly > 3 wt.%, Fe2O3 total/MgO mostly > 2), Cr (often > 100 ppm) and Ni (often > 10 ppm).
40	UK	Jurasic rocks, London–Brabant platform

concentrations (high SD), while Y has the lowest concentrations and the lowest range of values (low SD). Although La and Y have similar median values for total concentrations (XRF-total), the median values for the extractable La (aqua regia) are significantly higher (Table 1).

**Table 3**

Explanation of the numbered lanthanum anomalies in the interpolated maps for agricultural soil (AP) (in mg/kg) analyzed by ICP-MS.

La Anomaly (Ap)	Country	Explanation of the anomalous values
1	Finland	Peat soils, varying bedrock
2	Finland	Clay soils, association with large anomaly in regional till geochemistry, metasedimentary or granitic rocks
3	Finland	Clay soils with granite–pegmatite–magmatic bedrock
4	Sweden	Clay minerals, graywacke, sandstones, schists. Sulfide mineralization in Bergslagen e.g., Jadersbruk sulfide W, Pb, Zn, Cu, Ag sulfide and calc silicate skarn
5	Sweden	Granite–pegmatite–migmatite bedrock
6	Sweden	Paleoproterozoic intrusive rocks (granite–quartz monzoite association with some small anallite mineralization)
7	Sweden	Carbonatite and nepheline syenite in the Alnö Area
8	Norway	Sveconorwegian granitoid, granite, pegmatite
9	Norway	Sveconorwegian granitoid, granite, pegmatite
10	Sweden	Younger granite, Sveconorwegian in age, and Soliden W–Fe skarn mineralization
11	Sweden	Younger granite–pegmatite in Sveconorwegian orogen
12	UK	Paleozoic–Precambrian metamorphic rocks, Faeroes–Shetland–Orkney basin,
13	Germany	Tertiary (Oligocene–Miocene) volcanics of Kuppenrhön (Wasserkuppe near Abtsroda)
14	Sweden	W mineralization in skarn and granite bedrock
15	France	Tertiary–Quaternary cover including paleosoil, Fe-rich Tertiary soil
16	Portugal	Paleozoic intrusive rocks, Iberian Massif
17	Portugal	Paleozoic intrusive–metamorphic rocks, Iberian Massif
18	Spain	Paleozoic intrusive–metamorphic rocks, Iberian Massif
19	Spain	Paleozoic intrusive–metamorphic rocks, Iberian Massif
20	Spain	Possibly due to Iberian massif, Paleozoic intrusive rocks and some Jurasic–Neogene volcanic rocks belong to Alentejo–Guadalquivir Basin
21	Spain	Silurian–Ordovician rocks, Iberian Massif
22	France	Black marls and Permian unconformity (Fe, Mn, ..)
23	France	Silesian coal
24	France	Some ancient industrial site (coal) and salt brine. Contamination ?
25	Italy	Southern Tuscany alkaline volcanics
26	Italy	Latiun alkaline volcanics
27	Italy	Alkaline volcanics of Campania region
28	Italy	Anthropogenic source. In the area there are discontinued petrochemical industries (Priolo–Siracusa) and intense agricultural activity (Avola)
29	Italy	Igneous and metamorphic pre-Alpine basement
30	Italy	Anthropogenic source. The anomalies occur in the Taranto area, where steel industries are present, and intense agricultural activity as well
31	Italy	Old residual red soil – Terra Rossa
32	Croatia	Precambrian and Paleozoic schists
33	F.Y.R.O.M.	The most likely source of the elevated La value (39.597 mg/kg) is the phosphorite, lignite and/or the Pliocene lacustrine sediments with material derived from the phosphorite and lignite.
34	Greece	Precambrian gneisses
35	F.Y.R.O.M.	Terra Rossa residual soils over carbonate rocks – Terra Rossa. Bauxite deposits
36	Bosnia & Herzegovina	High-potassic (high K–Mg) plutonites–Durbachite (Certovo bremeno suite).
37	Czech Republic	High-potassic (high K–Mg) plutonites–Durbachite (Certovo bremeno suite).

This indicates that Y resides in phases which are more resistant to leaching than La does. This difference is determined by the mineralogy of the collected samples and the underlying lithologies from which these soils were derived. Lanthanum occurs in trace amounts in rock forming minerals which are more prone to weathering (and therefore leaching) than Y-bearing minerals. Lanthanum also occurs in several minerals, from common rock forming minerals such as micas and feldspar to accessory phases (e.g., monazite) while Y generally occurs in resistant accessory minerals (e.g., zircon, xenotime), but can occur as trace element in hornblende, clinopyroxene, garnet and biotite.

**Table 4**

Explanation of the numbered yttrium anomalies in the interpolated maps for agricultural soil (Ap) (in mg/kg) analyzed by ICP-MS.

Y anomaly (Ap)	Country	Explanation of anomalous values
1	Finland	Peat soils, varying bedrock
2	Finland	Clay soils, metasedimentary rocks
3	Finland	Clay soils with granite–pegmatite–magmatic bedrock
4	Sweden	Clay minerals, graywacke, sandstone, schist. Sulfide mineralization in Bergslagen e.g. Jadersbruk sulfide W, Pb, Zn, Cu, Ag and calc silicate skarn
5	Sweden	Granite–pegmatite–magmatic bedrock
6	Sweden	Paleoproterozoic intrusive rocks (granite–quartz monzoite association with some small analite mineralization)
7	Sweden	Younger granite, Sveconorwegian in age, and Soliden W–Fe skarn mineralization
8	Sweden	possibly due to W-mineralization in skarn and granite bedrock
9	Germany	Permian Basin with acid volcanic rocks (Stockheimer basin in southwest of the Frankenwald)
10	UK	London–Brabant platform, Jurassic rocks
11	UK	Paleozoic–Precambrian metamorphic rocks (Faeroes–Shetland–Orkney basin)
12	Ireland	Paleozoic intrusive rocks and undivided Precambrian rocks (Ireland–Scotland platform)
13	UK	Paleogene sedimentary units
14	France	Tertiary–Quaternary cover including paleosoil, Fe-rich Tertiary soil
15	Portugal	Paleozoic intrusive rocks, Iberian Massif
16	Spain	Cambrian intrusive, Tajo-Duero basin
17	France	Black marls enriched in LREE, Lower–Middle Jurassic
18	France	Permo-Tertiary unconformity with F, Ba, and REE enrichment, northern margin of the Morvan shield.
19	France	Some ancient industrial site (coal) and salt brines. Contamination?
20	Italy	Latinum alkaline volcanics
21	Italy	Small bauxite deposits of Alta Murgia (Apulia Region).
22	Italy	Intense agricultural activity.
23	Italy	Intense agricultural activity and ion-adsorption in clay-rich soils.
24	Italy	Small bauxite deposits of the Otranto area (Apulia Region).
25	Slovenia	Carboniferous sediments
26	Croatia	Old residual red soil – Terra Rossa
27	F.Y.R.O.M.	Precambrian schists and gneisses
28	Greece	The most likely source for the elevated Y value (31.843 mg/kg) is the phosphorite, lignite and/or the Pliocene lacustrine sediments with material derived from the phosphorite and lignite
29	Greece	Residual soil on Turonian to Palaeocene limestone; also there are flysch sediments of Upper Albian to Coniacian age nearby. From the available geological information, it is difficult to explain the elevated Y value of 31.615 mg/kg from natural geological causes, apart from the clayey nature of the residual soil developed on limestone, and unless there is some input from the flysch formation, which may also explain the elevated Au value (0.009297 mg/kg). Another likely source for the elevated Y is from NPK fertilizers, since olive trees are cultivated on the agricultural site.
30	Bosnia & Herzegovina	Ash with increased U content (age 17.0 Ma)

The abundance of La in granitic rocks is much higher than that of Y. The latter, together with heavy REEs, forms more stable compounds than La (with other light REEs) and this inhibits its mobility in surficial environment and resulting low extractability. The adsorption to clay is higher for La than Y, enhancing the La concentrations in clay-rich soils.

Cerium and La show similar geochemical behavior with Ce being more abundant. Both elements are major constituents of monazite, a common accessory mineral and the main repository of REEs in crustal rocks. Lanthanum and Ce occur as minor elements in a large variety of other minerals, silicates, fluorides, phosphates, carbonates. Both Ce

and La are enriched in fine-grained sedimentary rocks with high clay content.

The elemental distribution of La, Ce and Y implies that alkaline soils with high pH tend to have higher REEs contents, e.g., soils developed on carbonates can be enriched in REEs. Distribution of La and Ce anomalies in Ap (Figs. 2 and 3) and Gr (ESMs 2 and 4) soils is similar, and can be attributed to the geology of the area and chemical processes (leaching, pH, redox conditions) in soils. Anomalies in Ap which do not overlap with Gr anomalies (ESMs 2 and 4) are thought to have an anthropogenic origin (e.g., from fertilizers).

Apart from few exceptions (e.g., in the UK, southern France), Y anomalies tend to be more abundant in Gr than in Ap soils (Fig. 4, ESM 6), which can be explained by the higher immobility of Y, remaining fixed in the deeper horizons of undisturbed soils. This suggests a geological source for the anomalies.

In summary, La has the highest extractability and displays the largest difference between maximum concentrations in Ap and Gr soils for both analytical methods used (aqua regia and total), while Y shows the lowest extractability and small differences between Ap and Gr soils. Cerium has intermediate extractability of ca 50% and shows no difference between maximum values in Ap and Gr soils.

### 3.3. Exploring new patterns in the ratio map

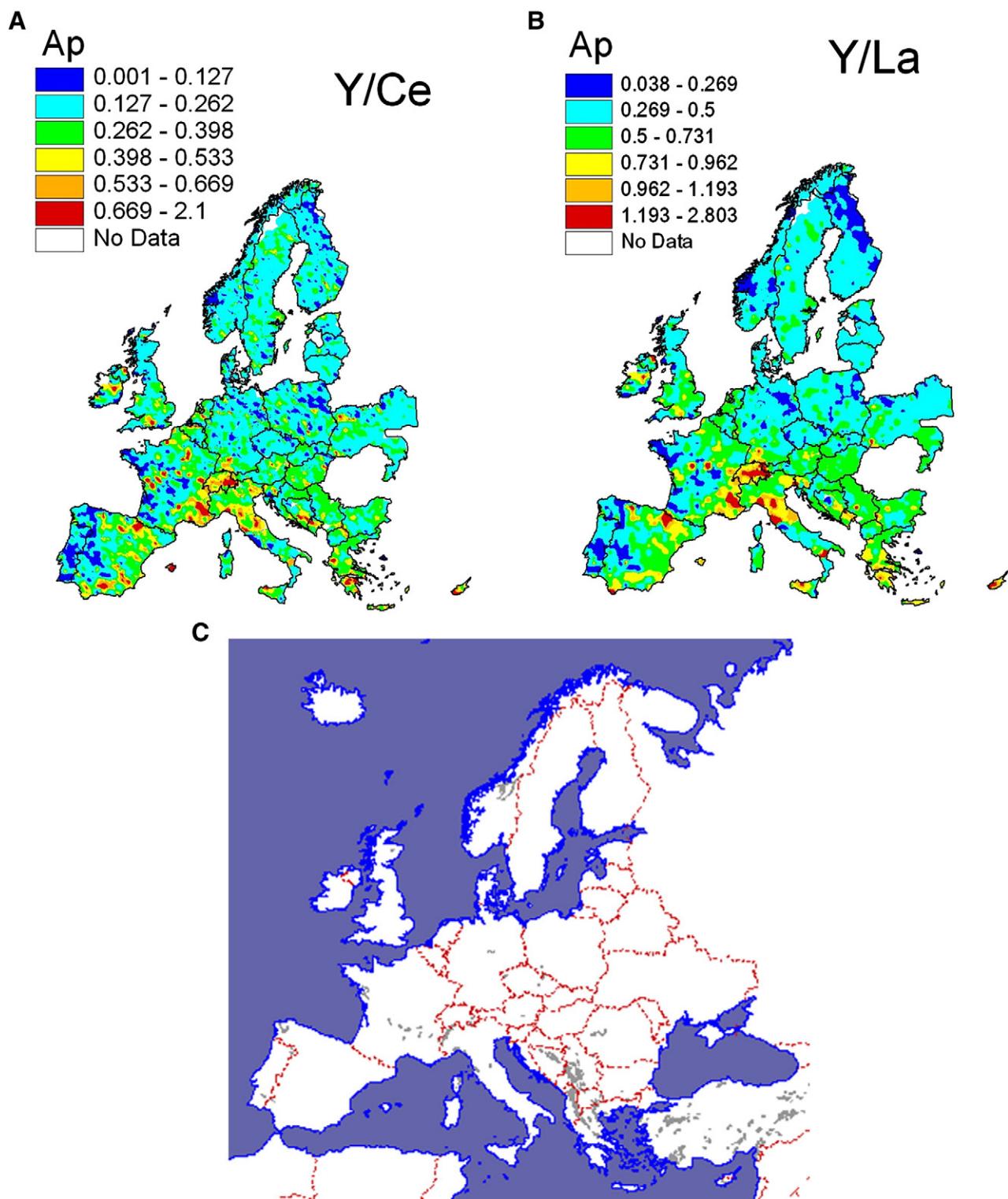
Elemental ratios maps of soils have been used for long time in environmental and exploration geochemistry (Brand, 1999). The use of element ratios in geochemical exploration can help to distinguish mineralized from barren geological complexes, predict geological units, and provide vectoring toward ore environments (Garrett et al., 2008). The elemental ratio maps have also been used in risk assessment, quantitative assessment of geochemical exploration techniques success (Stanley and Noble, 2008) and urban geochemistry (Cicchella et al., 2008). In this paper the ratio map of the Y/Ce and Y/La were produced to represent the ratios of HREEs vs LREEs (Fig. 6a, b).

In Europe several ophiolite complexes of different ages occur (Asch, 2003) (Fig. 6c). Ophiolites are a section of the earth's oceanic crust and the underlying upper mantle that has been uplifted and exposed above sea level, and often emplaced onto and over continental crustal rocks. Compared to mid-ocean ridge basalt (MORBs), ophiolites are selectively enriched in alkali and alkaline earth metals, and other incompatible elements (Pearce et al., 1984; Shaikh et al., 2005). Some studies of the geochemistry of trace and REEs on ophiolites reported LREE depletion and high Zr/Nb ratios. Similar REE patterns have been reported from various extensional settings (Gariepy et al., 1983; Hebert et al., in press; Massey, 1983; Saunders et al., 1982). In many cases, in those rocks, the REEs (mainly HREEs) do not change significantly during sea floor hydrothermal alteration and regional metamorphism (Polat and Hofmann, 2003). However, some studies have shown that high temperature alteration and high-grade metamorphism modify the concentrations of REEs and immobile elements (Jiang et al., 2005).

In our study, it is clear from the spatial distribution that the high ratios of Y/Ce and Y/La are strongly correlated to the occurrences of ophiolites and in some cases reflecting the alkaline and carbonate rocks in Europe. This hypothesis can be used as a tool in regional mapping and/or prospecting.

### 3.4. Comparing the FOREGS and GEMAS

The visual comparison of FOREGS and GEMAS distribution maps is rather difficult due to the different sample density and high degree of map generalization. Instead, Table 5 reports a summary of basic statistical parameters for comparing La, Ce and Y in GEMAS (both in aqua regia and XRF) and topsoils media of FOREGS data base (aqua regia). Because of the similar origin of GEMAS and FOREGS topsoil data, in this paper we focus on comparing only those datasets. The FOREGS and GEMAS elemental maps share many common features, for example the main



**Fig 6.** Map of the Y/Ce ratio (a) and Y/La (b) in European agriculture soils and occurrence of ophiolites in Europe (modified from the IGME 5000, Asch, 2003).

division between northern and southern Europe (along the line of the last glacial maximum). In FOREGS maps (Fedele et al., 2008) the difference between northern Europe and the rest of the continent is however more visible than in GEMAS data, where numerous large positive anomalies occur on the Fennoscandian Shield.

Large Ce anomalies in clay-rich soils (Ap and Gr) in central Sweden and southern Finland are not seen in topsoil samples from FOREGS. The numerous positive La anomalies from Fennoscandian Shield present in Ap and Gr soils of GEMAS are not as pronounced in FOREGS project

dataset. Large La anomalies from northern Sweden and the Pyrenees Mts in FOREGS topsoils pattern are however lacking in GEMAS data. Yttrium anomalies show trends similar to those seen in the La and Ce distribution. The GEMAS soils do not show extensive Y anomalies in southern Sweden, northwestern Norway and western Ireland, as seen in FOREGS topsoil data. The Ce and La median values of FOREGS topsoils (total concentrations by ICP MS) are similar to GEMAS XRF-total results and 50% higher in comparison with the aqua regia digestion (Table 5). This clearly indicates the presence of resistant minerals (e.g. zircon,

**Table 5**

Summary statistics comparing Ce, La and Y from GEMAS database and topsoils media from FOREGS database.

Media	Unit	Min.	Max	Median	SD
La	Topsoil	mg/kg	1.1	143	23.5
	Ap (aqua regia)	mg/kg	1.0	109	14.3
	Ap (XRF-total)	mg/kg	10	155	23
	Gr (aqua regia)	mg/kg	0.9	229	13.6
	Gr (XRF-total)	mg/kg	10	269	24
	Ce	mg/kg	2.45	267	48.2
Ce	Topsoil	mg/kg	1.6	265	28.3
	Ap (aqua regia)	mg/kg	1.0	317	58
	Ap (XRF-total)	mg/kg	1.6	272	27.1
	Gr (aqua regia)	mg/kg	10	315	56
	Gr (XRF-total)	mg/kg	<3	267	21
	Y	mg/kg	0.2	64	6.6
Y	Topsoil	mg/kg	6	111	27
	Ap (aqua regia)	mg/kg	0.2	76	6.4
	Ap (XRF-total)	mg/kg	3	118	25
	Gr (aqua regia)	mg/kg	0.2	110	11.0
	Gr (XRF-total)	mg/kg	3	110	11.0

monazite, apatite, xenotime, titanite, rutile, garnet) in the sample material which cannot be easily leached by aqua regia solution.

The main difference between the GEMAS and FOREGS datasets can be seen in the extent of anomalies, those in the GEMAS maps are generally localized, while FOREGS anomalies have a larger extent, which may be a consequence of the lower sampling density and the interpolation technique used (see Lima et al., 2008). The resulting impression is that FOREGS geochemical data show large extended anomalies which are difficult to attribute to local phenomena while the GEMAS data shows aerially restricted anomalies that are easier to explain in terms of local geology, and appear to reflect real elevated levels of elements in a given region. Statistically, the FOREGS dataset is similar to the GEMAS results, with the median values of all sample media laying closer to the total contents GEMAS results (AR – aqua regia median values are ca two times lower for La and Ce and 4 times lower for Y).

#### 4. Conclusion

The study of Ce, La, and Y shows that the median values observed for the agricultural soils of Europe (Ap horizon, 0–20 cm) are close to those found in the grazing land soils (Gr samples, 0–10 cm). The main difference between the elemental distribution of La, Ce and Y is more closely related to the geochemical behavior of the individual elements and their extractability as affected by the source of the element in the sample media. Elemental distribution of La, Ce and Y implies that alkaline soils with high pH tend to have higher REE contents, e.g., soils developed on carbonates can be enriched in REEs. In some cases the anomalies are found to be related to phosphate and REE mineralization.

Comparing FOREGS and GEMAS data is not an easy task, however, in general the FOREGS and GEMAS elemental maps share many common features, such as the main division between the northern and southern Europe (along the line of the last glacial maximum). On FOREGS maps, the difference between northern Europe and the rest of the continent is however more visible than in GEMAS data, where several strong anomalies occur on the Fennoscandian Shield. In general, the FOREGS maps show exaggerated anomalies while in GEMAS elemental anomalies form confined maxima, often related to single or only a few sample points. FOREGS geochemical data shows large extended anomalies which are difficult to attribute to local phenomenon while the GEMAS restricted anomalies are easier to explain and seem to reflect more the geogenic source in a given region.

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## Rare earth element distribution and mineralization in Sweden: An application of principal component analysis to FOREGS soil geochemistry

### ***Sammanfattning av artikel 2***

FOREGS (Forum of European Geological Surveys) databas har använts för att studera innehållet av sällsynta jordartsmetaller i fasta provmedia. Analysresultat för sällsynta jordartsmetaller i ytlig jord (topsoil) och dess underlag (subsoil) samt älvsediment (stream sediment) användes för att identifiera bakgrundsvärden för sällsynta jordartsmetaller i de olika provtyperna. Ett huvudsyfte med undersöningen var att jämföra bakgrundsvärdena av sällsynta jordartsmetaller i Sverige med de europeiska halterna av sällsynta jordartsmetaller. Det kunde fastställas att underliggande geologiska material (vanligtvis berggrunden och lösa avlagringar) är de viktigaste faktorerna som styr innehållet av sällsynta jordartsmetaller i jordar, och därför ges en utförlig presentation av de stora bergartsenheterna i Sverige. En faktor som också styr fördelningen av sällsynta jordartsmetaller i jord är mineraliseringar. Kartan avseende mineraliseringar med sällsynta jordartsmetaller sammantälldes för att visa sambandet mellan dessa och berggrundens litologi.

Kända mineraliseringar med sällsynta jordartsmetaller i Sverige har kategoriseras efter de genetiska modeller som gett upphov till de olika typerna av mineraliseringar. Dessa beskrivs som hydrotermal Bastnäs-typ, sällsynta jordartsmetaller associerade med apatitjärnmalm, sällsynta jordartsmetaller associerade med alkalina komplex, sällsynta jordartsmetaller associerade med fosforit, sällsynta jordartsmetaller associerade med syenit, sällsynta jordartsmetaller och uran i pegmatit och, slutligen, sällsynta jordartsmetaller i kvartsitanrikade vaskavlagringar.

Interpolerade kartor över koncentrationen av sällsynta jordartsmetaller baserade på FOREGS dataset har tagits fram och anomalier och höga koncentrationer av sällsynta jordartsmetaller i Sverige beskrivs och jämförs med de europeiska halterna. Generellt visar den lätta gruppens element (LREE) god korrelation med varandra och detsamma gäller för den tunga gruppens element (HREE), men grupperna korrelerar inte nödvändigtvis med varandra. Principalkomponentanalys (PCA) har tillämpats och resultatet avslöjar två grupper av associationer: en som representerar LREE och den andra HREE. Sammansatta färgkort baserade på PCA speglar särskilda litotektoniska domäner, speciellt tillhörande den arkeiska berggrunden i norra Sverige, den svekokarelska orogenens yngre fas samt unga graniter i sydväst. Även REE tillhörande lerbältet längs kusten i östra Sverige avspeglas i viss mån på PCA-kartorna.

### ***Summary of Paper 2***

In this paper, FOREGS data have been investigated with focus on rare earth elements in different solid media (topsoil, subsoil and stream sediments) to identify the background value of rare earth elements in the different solid media. One of the main aims of this paper was to compare the background value of Swedish rare earth elements in different solid media with the European level. It was concluded that the underlying geological material (generally bedrock or superficial deposit) is the major factor controlling the rare earth element content in soil. Therefore, a comprehensive introduction to the Swedish bedrock geology was included in this paper. Another main factor that controls the distribution of rare earth elements in soil is mineralisation. Therefore, a map on the mineralisation of rare earth elements was prepared to visualise the relationship between rare earth elements content in bedrock lithology and mineralisations.

Known rare earth element mineralisations were categorised based on genetic models, and are described as hydrothermal Bastnäs-type, REEs association with apatite iron, REE associated with alkaline rocks, REE associated with phosphorite , REE associated with syenite, pegmatite containing uranium and REE and, finally, quartzite enriched REE in paleoplacer deposits.

Interpolated maps of rare earth element concentrations based on the FOREGS database have been produced, and the anomalies or higher concentration of rare earth elements are described in respective map and compared with the European concentrations of rare earth elements. Generally, light rare earth elements (LREE) show good correlation with each other and the same is the case for

the heavy rare earth elements (HREE), but the two groups do not necessarily correlate with each other. Principal component analysis (PCA) was applied and the result reveals two groups of associations: one representing LREE and the other representing HREE. Color composite maps derived from PCA also seem promising to reflect main lithotectonic domains especially Archaean rocks in the northern Sweden, younger phase of Svecokarelian orogen, and young granites in the southwest. REE in the clay belt along the coast in eastern Sweden is also discernible at the PCA maps.

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## Rare earth element distribution and mineralization in Sweden: An application of principal component analysis to FOREGS soil geochemistry

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### ABSTRACT

This paper presents results of statistical analyses and spatial interpretations of distributions of rare earth elements (REEs) in Sweden using the Forum of European Geological Surveys (FOREGS) geochemical database of topsoil, subsoil and stream sediment compositions. Raster maps depicting spatial distributions of individual REEs were created by interpolation of uni-element data and then principal component (PC) analysis was carried out on the REE data to identify geochemical anomalies associated with bedrock lithology and known mineralizations. The spatial distributions of REEs in Sweden are studied using only the Swedish data subset and the entire European data set. The light rare earth elements (LREEs) La, Ce, Nd and Sm show good correlations among each other but not with Eu. The heavy rare earth elements (HREEs) including Tb, Dy, Ho, Er, Tm, Yb and Lu also show good correlations among each other but not necessarily with the LREE. La, Ce and Nd are the most abundant REEs in all the studied media (topsoils, subsoils and stream sediments), with average median concentrations of 25.3 mg/kg, 53.6 mg/kg and 23.9 mg/kg, respectively. The total explained variances of the first two PCs of each of the REE dataset for topsoils, subsoils, and stream sediments are 95.4%, 95.8% and 95.2%, respectively. Biplots of the first two PCs of each of the REE dataset for topsoils, subsoils, and stream sediments commonly reveal two distinct groupings – HREEs and LREEs – whereas biplots of PC1 versus PC3 of these datasets commonly reveal three distinct groupings – Eu, Ce and other REEs. The main difference between the distribution patterns of LREE and HREE is likely due to enrichment of the LREEs in the Archean bedrock underlying northern Sweden. HREE concentrations in the Archean to Paleoproterozoic metasediments are rather low. Color composites of PC maps produced from the topsoil and subsoil datasets clearly reflect the Archean rocks in northern Sweden and outline the second phase of the Svecokarelian orogen.

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### 1. Introduction

The FOREGS (Forum of European Geological Surveys) Geochemical Baseline Mapping Program was originally planned as the European contribution to the global geochemical dataset, and as a guideline for carrying out such a complex international survey on the continental scale (Salminen et al., 2005). The main objectives of FOREGS were to provide a basis for formulating policies and legislation concerning the management of harmful elements and to define their corresponding safety levels (Salminen et al., 2005). Therefore, the FOREGS initiated a program to construct a standardized geochemical database with the aim of compiling the first geochemical atlas of Europe (Fedele et al., 2008). As a result, a large geochemical database is now available free for public use (De Vos et al., 2006;

Salminen et al., 2005). The FOREGS database covers 26 countries and contains descriptions for various environmental media (soils, stream and floodplain sediments, and water) that were chemically analyzed for more than 70 elements including the rare earth elements (REEs).

The REEs comprise 15 chemically similar metallic elements, which are a key group of trace elements for the geochemical study of earth systems (Prego et al., 2009; Taylor and McLennan, 1985). The REEs are commonly divided into the light rare earth elements (LREEs) with lower atomic weights and larger atomic radii (lanthanum to europium), and the heavy rare earth elements (HREEs) with higher atomic weights and smaller atomic radii (gadolinium to lutetium). This gradual decrease of atomic radii with increasing atomic number is a characteristic feature of REEs and it is known as contraction of lanthanides. Scandium and yttrium are often grouped with the REEs because the former is chemically similar to the latter (Hedrick, 1997; Walters et al., 2011). In particular, yttrium is often grouped with the HREEs because of its similar chemical properties (Samson and Wood, 2004).

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The REEs are not found as native elements but as a variety of minerals, e.g., oxides (fergusonite), carbonates (bastnäsite), phosphates (monazite), and silicates (allanite). At least 100 minerals can incorporate REEs into their crystal structures while approximately 10 of these minerals contain significant REE concentrations. Currently, only bastnäsite, monazite, and xenotime are the primary REE-bearing minerals of economic importance (Richardson and Birkett, 1996).

The REEs are incompatible during most magmatic processes and, thus, concentrate in the final products of magma differentiation (e.g., evolved granites and pegmatites). The REEs have been considered relatively immobile during metamorphism and, in the surficial environments, are not easily affected by alteration (Öhlander et al., 1996). However, some studies have indicated that the REEs can be mobile during weathering processes, e.g., in till cover in northern Sweden (Öhlander et al., 1991, 1996).

The most significant economic concentrations of REE-bearing minerals worldwide are hosted in or associated with alkaline igneous rocks and carbonatites. Within hydrothermal systems, REE-bearing minerals are associated with quartz and fluorite-bearing veins and as breccia filling. REE-bearing minerals also occur in skarns, in pegmatite and are sometimes concentrated in placer and laterite clay deposits. The geological setting of economic concentrations of REE-bearing minerals is usually within, or a combined variety of these rock types and mineralizing events. REEs are also extracted as a by-product during uranium and niobium milling process (Pell, 1996).

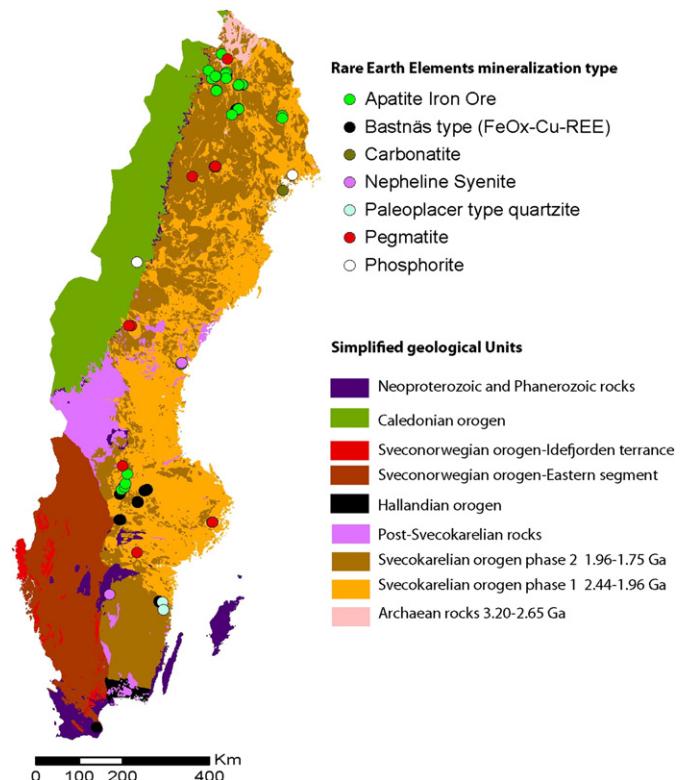
During the last few decades, rare earth metals have found many applications in metallurgy, electronics, the high-tech industry, medicine, military, and many other areas of modern life. There is, therefore, a need to define the natural background levels of REEs in order to distinguish their natural variations related to geology and mineralization from anthropogenic input and contamination (Fedele et al., 2008).

The main objective of this paper is, therefore, to analyze the distributions of REEs in Swedish subsoils, topsoils, and stream sediments using the FOREGS database to identify patterns that could be related to bedrock geology and mineralization. For this, we apply the principal component analysis to study the structure and spatial distribution of the Swedish REE data in respect to the regional geology (underlying bedrock type) and mineralizations.

## 2. Geological and tectonic setting of Sweden

Geographically, Sweden can be divided into seven geological regions, each with a distinct tectonic history and geochemical character (Fig. 1). Most of these regions belong to the Fennoscandian Shield, which includes the Archean rocks of northern Sweden, the Svecokarelian Orogen, post Svecokarelian rocks of the Trans-Scandinavian Igneous Belt, the Bleckinge–Bornholm Province and the Sveconorwegian Orogen. Impinging on the western side of Sweden, and incorporating many reworked components of the Fennoscandian Shield, is the Caledonian Orogen; whereas younger intrusives and outliers in the sedimentary cover in southern Sweden are collectively grouped here as the Phanerozoic Rocks.

Archean Rocks occur exclusively in northern Sweden (Norrbotten County) and are composed of ca. 3.5–2.5 Ga tonalite–trondhjemite–granodiorite gneisses, paragneisses, greenstone, granulite and migmatitic amphibolites. Most of these units were generated during the Saamian orogeny (3.1–2.9 Ga), amalgamated by collision at ca. 2.0–1.9 Ga, then reworked during Proterozoic tectonic events to form collisional belts such as the Lapland granulite belt (Hölttä et al., 2008). The southernmost outcrops of Archean rocks occur between Luleå and Piteå, near Boden, and towards Jokkmokk; however, they are thought to underlie the Palaeoproterozoic rocks located southwards. Products of mafic volcanism associated with the breakup of the early Archean crust in the early Palaeoproterozoic are preserved in the greenstone belts of northern Sweden.



**Fig. 1.** Simplified geological map of Sweden with main types of REE deposits (based on data from Geological Survey of Sweden).

The majority of Sweden consists of rocks of the Svecokarelian Orogen, formed during the Palaeoproterozoic in two distinct phases, one during 2.44–1.96 Ga and the other 1.96–1.75 Ga. Earlier phases of the orogen were marked by mafic volcanism probably associated with the breakup of the early Archean crust. The majority of the orogen is assembled from a series of island arc terranes and interlying sedimentary basins accreted onto the Archean continental core. All units were variably metamorphosed with grades reaching amphibolites–granulite facies, with many rock units showing extensive migmatization. Thus, before ca. 1.7 Ga, almost the entire Fennoscandian Shield experienced extensive metamorphic and magmatic activities, which resulted in magmas ranging from anatetic S-type granites to various mantle-derived melts, and the formation of migmatites and shear zones (Högdaal et al., 2004; Korsman et al., 1999). The youngest events in the Svecokarelian orogen are the deposition of the Jotnian sandstone in the Bothnian Gulf at ca. 1.5–1.2 Ga and much of the region has been extensively intruded by basic dykes.

The Trans-Scandinavian Igneous Belt (TIB) is situated to the west of the Svecokarelian domain and stretches from southernmost Sweden northwards, beneath the Caledonian mountain chain and up to the coastal regions in northern Norway (Högdaal et al., 2004). Within the Caledonides, the TIB rocks outcrop in tectonic windows, e.g., the Grong–Olden Culmination. The belt consists largely of undeformed granitoids and associated volcanic rocks formed in at least three different episodes (TIB 1, TIB 2, and TIB 3) between ca. 1.85 and 1.65 Ga, with youngest intrusions at ca. 1.4. In places, the TIB is partly covered by the Jotnian sandstone and cut by diabase dykes (1.25–1.2 Ga and 1.0–0.9 Ga).

The Bleckinge–Bornholm province is located in southern Sweden. Early amphibolites, felsic metavolcanics, mica schists, and gneisses (ca. 1.77–1.69 Ga) were intruded by tonalite–granodiorite plutons and were not affected by the Sveconorwegian orogeny. Mesoproterozoic rapakivi granites (1.5–1.25 Ga), pegmatites, gabbros, mafic dykes and associated bimodal volcanic rocks represent younger units (Bingen et al., 2008; Lahtinen et al., 2008).

The Sveconorwegian orogen predominantly consists of bedrock originally formed during the Gothian orogeny (1.7–1.55 Ga), cut by late Mesoproterozoic igneous rocks (ca. 1.1–0.9 Ga), and subsequently deformed and metamorphosed under amphibolite to granulite–eclogite facies conditions into gneisses, granulites, eclogites, and migmatites. Rare supracrustal rocks (greywacke, quartzite, shale) occurring with minor mafic to felsic volcanics in southwestern Sweden have been metamorphosed under greenschist to amphibolites facies conditions. The Sveconorwegian units are intruded by several generations of diabase with the youngest ones dated at ca. 615 Ma (Göteborg diabase). The orogen is divided into several N–S-trending segments separated by ductile deformation zones such as the Mylonite Zone separating Eastern and Western segments (Andersson et al., 2002).

Neoproterozoic rocks in Scandinavia are represented by sedimentary successions of marine and fluvial sandstones, conglomerates, and carbonates occurring within the Caledonides. Dolerite dyke swarms (ca. 600 Ma) cut voluminous siliciclastic successions and mark the opening of the Paleozoic Iapetus Ocean. Ediacaran glaciations resulted in tillite formation and postglacial marine sediments (Nystuen et al., 2008). Outside the Caledonides, Neoproterozoic rocks occur locally in southern Sweden by the lake Vättern (sandstone, shale, dolomite, and conglomerate) and in central Sweden (Alnö carbonatite complex) (Nystuen et al., 2008).

The Caledonian orogen was formed during the Early–Mid Paleozoic (Ordovician to Devonian) when North America and Greenland

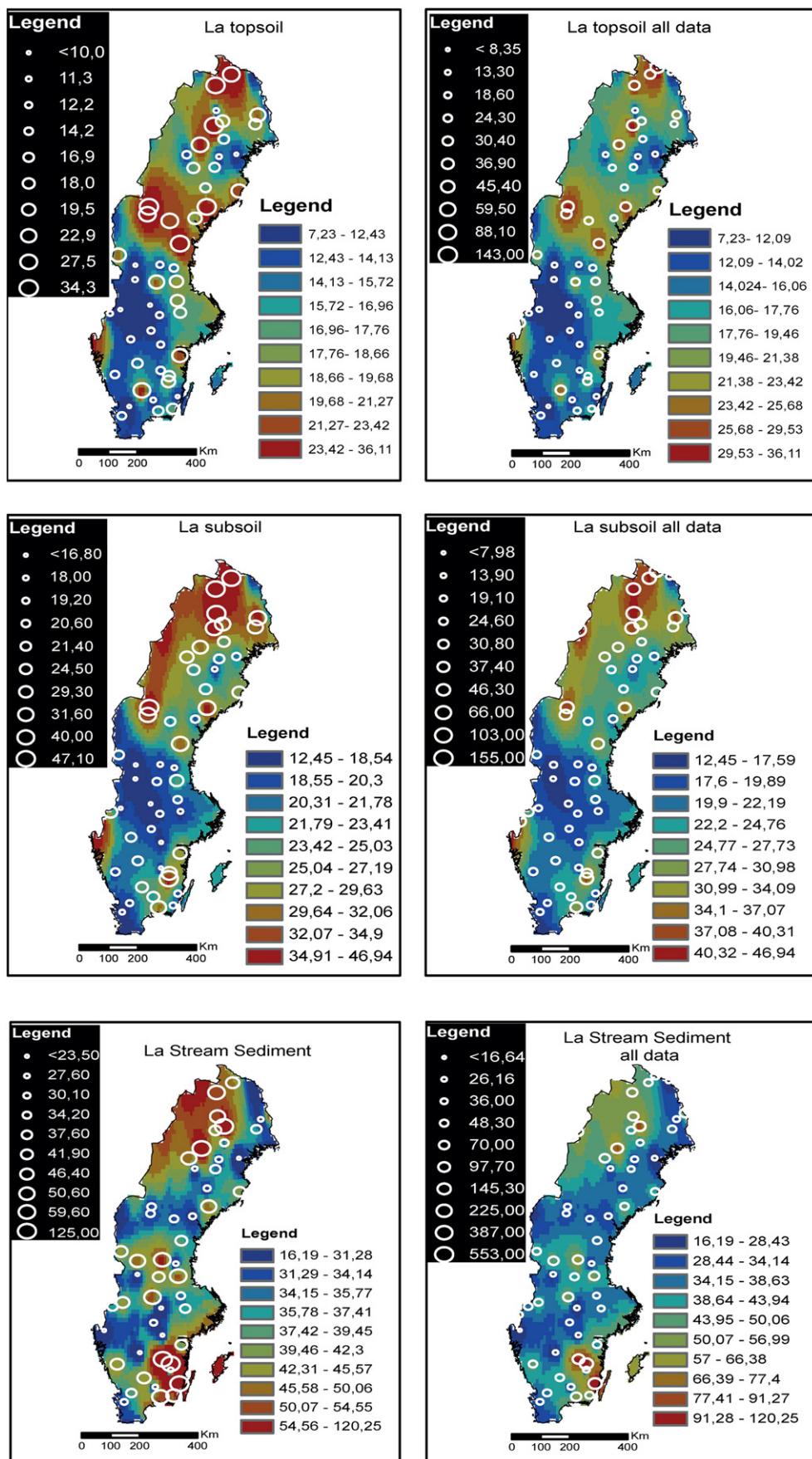
(Laurentia) collided with Scandinavia (Baltica). In Sweden, the current exposures are mainly composed of Neoproterozoic to Paleozoic (mostly Silurian) marine to fluvial sediments and volcanoclastic successions, which were deposited at the continental margin of the Iapetus Ocean between ca. 700 and 400 Ma (Gee et al., 2008). Together with slices of older basement, these rocks were thrust several hundred kilometers eastwards onto the Fennoscandian shield in several large thrust sheets (nappes) (Gee et al., 2008). Within Caledonian nappes, the metamorphic grade varies from lower greenschist to granulite–eclogite facies (Gee et al., 2008).

Outside the Caledonides, the majority of Phanerozoic Rocks are remnants of the Cambro–Silurian sedimentary cover (550–400 Ma old sandstones, shales, and limestones) that once covered much on central and northern Europe. These are found in southern and central Sweden, e.g., near Östersund, Siljan, Billingen–Kinnekule, Skåne, and on the islands of Gotland and Öland. Cambrian to Permian diabase dykes, porphyritic monzonite, and ultramafic intrusions outcrop in central (Västergötland), western (Bohuslan), and southern (Skåne) Sweden. Triassic through Cretaceous shallow marine sandstones, siltstones shales, and limestones occur only in the south of the country.

All geological regions in Sweden have a variable but generally rather thin soil layer dominated by glacial debris from the last glaciation and marine or post-glacial deposits. The composition of glacial debris is mainly sandy till, especially common above the pre-isostatic rebound coastline. In central Sweden, heavy glacial or postglacial clays are

**Table 1**  
Basic statistics of REE concentrations (in mg/kg) in European and Swedish samples.

Europe							Sweden								
	Media	Samples	Min	Max	Mean	Median	SD		Media	Samples	Min	Max	Mean	Median	SD
La	Subsoil	790	0.78	155	27.7	25.6	16.1	La	Subsoil	51	12.30	47.10	25.19	21.40	8.61
	Topsoil	852	1.10	143	25.9	23.5	15.8		Topsoil	51	6.92	34.30	17.42	16.90	6.69
	Stream	853	1.30	553	41.0	32.5	44.8		Stream	51	15.80	125.00	43.05	37.60	22.82
Ce	Subsoil	790	1.04	379	56.8	53.7	32.9	Ce	Subsoil	51	22.70	101.00	55.91	48.80	18.81
	Topsoil	852	2.45	267	52.2	48.2	31.3		Topsoil	51	13.80	83.00	37.67	34.80	15.69
	Stream	853	2.20	1080	83.0	66.6	88.6		Stream	51	36.60	301.00	94.80	77.40	54.31
Pr	Subsoil	790	0.14	32.9	6.50	6.04	3.66	Pr	Subsoil	51	2.93	11.40	5.94	5.37	2.04
	Topsoil	852	0.29	31.6	6.02	5.60	3.64		Topsoil	51	1.64	8.16	4.10	3.91	1.63
	Stream	853	0.30	125.0	9.22	7.35	10.20		Stream	51	4.38	36.10	11.38	9.76	6.53
Nd	Subsoil	790	0.46	111	24.2	22.4	13.40	Nd	Subsoil	51	12.00	41.10	21.86	19.20	7.37
	Topsoil	852	1.14	132	22.4	20.8	13.52		Topsoil	51	6.71	31.80	15.14	14.50	6.12
	Stream	853	1.10	524	36.6	28.2	41.30		Stream	51	17.30	139.00	44.68	37.90	25.29
Sm	Subsoil	790	<0.10	18.2	4.66	4.38	2.47	Sm	Subsoil	51	2.30	8.33	4.30	3.80	1.47
	Topsoil	852	0.23	30.0	4.28	3.96	2.63		Topsoil	51	1.37	6.01	2.98	2.76	1.15
	Stream	853	0.20	106.0	6.91	5.40	7.55		Stream	51	3.49	24.60	8.53	7.25	4.75
Eu	Subsoil	790	<0.05	4.66	0.92	0.84	0.52	Eu	Subsoil	51	0.36	1.58	0.84	0.78	0.28
	Topsoil	852	0.05	6.99	0.85	0.77	0.56		Topsoil	51	0.24	1.29	0.65	0.63	0.23
	Stream	853	0.05	7.06	1.15	1.01	0.73		Stream	51	0.57	3.39	1.37	1.25	0.58
Gd	Subsoil	790	<0.1	16.0	4.52	4.24	2.33	Gd	Subsoil	51	2.25	7.89	4.25	3.82	1.46
	Topsoil	852	0.2	36.0	4.20	3.85	2.66		Topsoil	51	1.15	6.40	3.07	2.89	1.12
	Stream	853	0.2	90.5	6.32	5.06	6.45		Stream	51	4.05	26.80	8.75	7.31	4.69
Tb	Subsoil	790	<0.02	2.36	0.68	0.64	0.34	Tb	Subsoil	51	0.36	1.17	0.67	0.61	0.21
	Topsoil	852	0.03	7.01	0.64	0.60	0.42		Topsoil	51	0.22	1.08	0.49	0.47	0.18
	Stream	853	0.02	14.50	0.96	0.79	0.93		Stream	51	0.65	4.26	1.28	1.03	0.68
Dy	Subsoil	790	<0.10	12.7	3.79	3.66	1.84	Dy	Subsoil	51	2.02	7.23	3.79	3.55	1.19
	Topsoil	852	0.18	44.9	3.58	3.42	2.40		Topsoil	51	1.48	6.18	2.95	2.94	0.94
	Stream	853	0.11	78.2	5.40	4.53	4.81		Stream	51	3.78	25.30	7.06	5.78	3.68
Ho	Subsoil	790	<0.02	2.58	0.75	0.74	0.37	Ho	Subsoil	51	0.37	1.47	0.78	0.75	0.24
	Topsoil	852	0.03	9.16	0.72	0.68	0.48		Topsoil	51	0.28	1.34	0.61	0.60	0.20
	Stream	853	0.04	16.70	1.09	0.92	0.97		Stream	51	0.74	5.49	1.47	1.20	0.79
Er	Subsoil	790	<0.10	7.42	2.20	2.18	1.06	Er	Subsoil	51	1.21	4.39	2.34	2.24	0.70
	Topsoil	852	0.12	26.00	2.10	1.98	1.37		Topsoil	51	0.95	3.96	1.88	1.80	0.58
	Stream	853	0.07	46.00	3.18	2.67	2.79		Stream	51	2.14	17.30	4.36	3.47	2.44
Tm	Subsoil	790	<0.02	1.08	0.33	0.31	0.16	Tm	Subsoil	51	0.17	0.65	0.36	0.36	0.11
	Topsoil	852	<0.02	4.03	0.31	0.30	0.20		Topsoil	51	0.13	0.57	0.28	0.28	0.08
	Stream	853	0.02	6.43	0.47	0.40	0.40		Stream	51	0.35	2.68	0.65	0.53	0.37
Yb	Subsoil	790	<0.05	7.37	2.17	2.13	1.02	Yb	Subsoil	51	1.28	4.37	2.48	2.40	0.75
	Topsoil	852	0.09	25.00	2.09	1.99	1.29		Topsoil	51	1.08	4.19	2.01	1.98	0.59
	Stream	853	0.10	42.8	3.09	2.58	2.65		Stream	51	2.26	18.70	4.56	3.76	2.55
Lu	Subsoil	790	<0.02	1.06	0.32	0.31	0.15	Lu	Subsoil	51	0.18	0.59	0.36	0.35	0.10
	Topsoil	852	<0.02	3.21	0.31	0.30	0.18		Topsoil	51	0.17	0.58	0.30	0.30	0.08
	Stream	853	<0.02	6.04	0.48	0.39	0.40		Stream	51	0.34	3.01	0.71	0.57	0.42



**Fig. 2.** Geochemical maps of La in topsoils, subsoils and stream sediments in Sweden. Symbol sizes and color scales for maps on the left are based on Swedish datasets, whereas those for map on the right are based on the whole European datasets.

common while peat lands occur frequently, especially in the northeast. Glacial deposits are strongly influenced by ice movement and post glacial reworking by melting waters. As a result, most of the deposits, especially till cover and fluvial sediments, have been displaced and redeposited. Ice transport distances are, however, short and rarely exceed 5–10 km in northern and central Sweden. In southern part of the country, displacement is more variable and can reach up to 60–80 km (Sohlenius et al., 2009).

### 3. REE mineralizations in Sweden

In Sweden, in many of the REE-bearing deposits were identified for the first time during the latter parts of the 19th century, most notably from the world famous Ytterby mine, from which the element ytterbium (Yb) derived its name. The elements cerium (Ce) and lanthanum (La) were discovered in minerals from Bastnäs and the Bastnäs region is still considered the most promising area for REE exploration in Sweden. REE-bearing mineral deposits occur in a broad range of igneous, sedimentary, and metamorphic rocks. Environments in which REEs are enriched can be broadly divided into two categories (Walters et al., 2011): (i) primary deposits associated with igneous and hydrothermal processes and (ii) secondary deposits concentrated from primary sources by sedimentary processes and weathering. Primary deposits include REEs associated with carbonates and/or alkaline igneous rocks, REEs associated with iron oxide–copper–gold (IOCG) deposits and hydrothermal deposits (unrelated to alkaline igneous rocks). Secondary deposits include marine placers (including coastal dune deposits formed by aeolian processes), alluvial placers, paleoplacers, lateritic deposits, and ion-adsorption clays (Walters et al., 2011). The main categories of REE mineral deposits in Sweden (Fig. 1), based on genetic sources, are described below.

- a) Hydrothermal *Bastnäs-type* ( $\text{FeO}-\text{Cu}-\text{REE}$ ). The main occurrences of the Bastnäs-type deposits are located in the Bergslagen mining district and are related to hydrothermal skarn mineralization in south-central Sweden (Holtstam and Andersson, 2007). Based on characteristic assemblages, the Bastnäs type deposits can be divided into two subtypes: LREE-enriched deposits located mainly in the Riddarhyttan-Bastnäs area, and deposits showing enrichment in LREE and Y + HREE mainly located in the Norberg district (Holtstam and Andersson, 2007).
- b) REEs associated with *apatite iron ore*. The magnetite–apatite deposits of the Kiruna district and surrounding regions of northern Sweden form the type locality for the magnetite–apatite end member of the IOCG deposit class (Barton and Johnson, 1996; Hitman et al., 1992). The characteristic feature of these deposits is a close association with sodic and potassic alteration (Frietsch et al., 1997; Martinsson, 1997) and anomalously high concentrations of the REEs (e.g., Frietsch and Perdahl, 1995). The main occurrences of REEs related to apatite iron ore is situated in Norrbotten County in the northern part of Sweden (the Kiirunavaara and Malmberget deposits) and in the Bergslagen mining district in central Sweden (e.g., Grängesberg). REEs usually reside in apatite (e.g., in the Kiirunavaara ore), which contain between 2000 and 7000 ppm REEs with a weak to moderate LREE/HREE enrichments and negative EU anomalies (Frietsch and Perdahl, 1995; Smith et al., 2007).
- c) REE related alkaline *carbonatite complexes*. Carbonatites are igneous carbonate rocks in which the modal percentage of carbonate exceeds 50% (Le Maitre, 2002). If the dominant carbonate is calcite, the rocks are classified as calcite carbonatites and are called sövite (coarse grained) or alvikite (fine grained) (Eckermann, 1948; Hornig-Kjarsgaard, 1998). Carbonates are considered

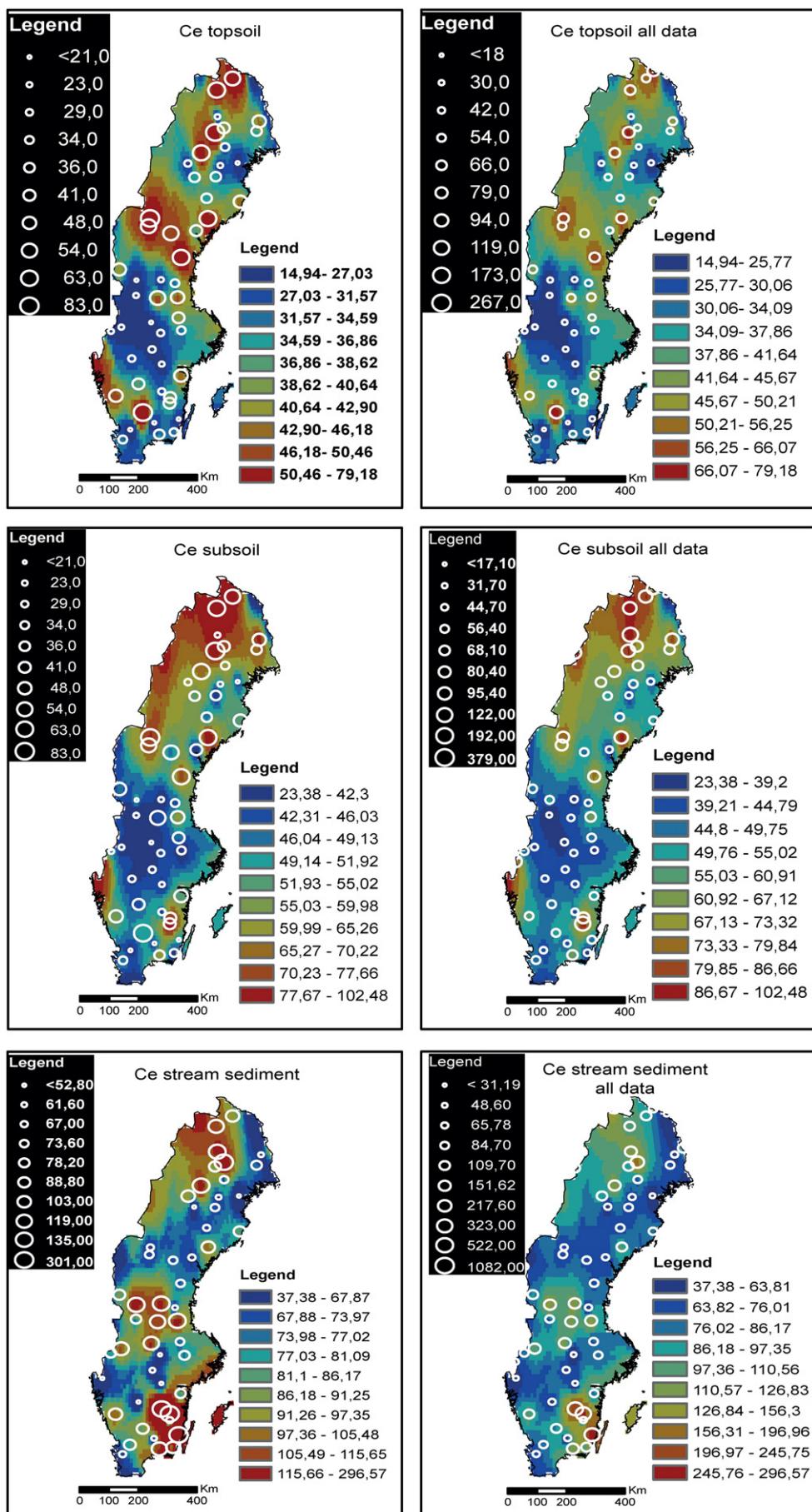
results of extreme fractionation of magmas. This process concentrates incompatible elements, including the REEs, into the final magmatic component, sometimes to economic levels (Hornig-Kjarsgaard, 1998). The LREEs show progressively greater degrees of enrichment over the slightly less mobile and heavier REEs. This, sometimes, result in extreme LREE/HREE enrichments (Balashov and Pozharitskaya, 1968; Eby, 1975; Kapustin, 1966; Kjarsgaard, 1998; Möller et al., 1980; Viladkar and Pawaskar, 1989; Von Maravic and Morteani, 1980). Some of the highest concentrations of REEs as a whole, and one of the strongest enrichments of LREEs over HREEs have been identified in sövite from the Alnö complex in Sweden (Hode Vuorinen and Hälenius, 2005; Kjarsgaard and Hamilton, 1989).

- d) *REE-U rich phosphorite* in Jämtland in central Sweden (Tåsjö). At the Caledonian front, in the lower allochthon, the Tåsjö uranium and REE mineralization is hosted by Paleozoic calcareous sandstone and shales with phosphorite overlying alum shale, which contains 0.03–0.07%  $\text{U}_3\text{O}_8$  and 0.11–0.24% total REE (Browne, 2008; David Gee, personal communication).
- e) *Peralkaline nepheline syenite*. Quartz undersaturated alkaline plutonic rocks with  $(\text{Na}_2\text{O} + \text{K}_2\text{O}) > \text{Al}_2\text{O}_3$ . The Norra Kärr deposits are hosted in an agpaitic complex (peralkaline nepheline-syenite) located by the lake Vättern in southern Sweden, 300 km southwest of Stockholm. The rocks comprising the Norra Kärr intrusion are very rare on a global scale, and include variety of rare minerals, particularly rich in REEs, zirconium, niobium, yttrium, and hafnium. According to the Tasman Metals Ltd report (2011), the size of the deposit has been estimated as 60.5 Mt averaging 0.54% total rare earth oxide with 53% of that being heavy rare earth oxide.
- f) *Pegmatites* containing U and REE bearing minerals are common but generally too small or too low in grade to be commercially exploited. Production of REEs from pegmatites mined for other minerals, such as feldspar or mica, is possible however. Allanite bearing pegmatites are relatively common and generally have high LREE/HREE ratios (Castor and Hedrick, 2006). Smeds (1990) carried out a comprehensive study on accessory minerals related to pegmatites in Sweden and classified pegmatites occurring in Svecokarelian rocks into two main groups: tourmaline  $\pm$  Li-mineral bearing pegmatite occurring in low- to medium-grade metamorphic rocks; and pegmatite bearing Y-REE-mineral type, which can be formed in several settings.
- g) *Paleoplacer type quartzite*. The most important placer deposits containing significant quantities of REE minerals are tertiary or quaternary in age. Orris and Grauch (2002) have identified more than 360 placer deposits worldwide. However, deposits as old as Precambrian (paleoplacers) are known and are found only in a few countries (Castor and Hedrick, 2006). The most important REE-bearing mineral in placer deposits is monazite, with minor quantities of xenotime, fergusonite, euxenite, samarkite, allanite, knopite, pyrochlore, and loparite (Möller, 1986). Several considerably older deposits containing REE-bearing minerals of possible Paleoproterozoic origin occur in southern Sweden in Västervik county (e.g., the Klockartorpet and Trostad mineralizations), and normally consist of a metamorphosed Proterozoic conglomerate containing REE bearing minerals.

### 4. FOREGS data—sampling and analytical methods

The field sampling, laboratory sample preparations and analytical methods of the FOREGS data are described in detail in Sandström et al. (2005). The FOREGS sampling grid (Salminen et al., 1998; Tarvainen et al., 2005) was based on the Global Terrestrial Network grid cells developed for the purpose of Global Geochemical Baselines Mapping (Darnley et al., 1995).

**Fig. 3.** Geochemical maps of Ce in topsoils, subsoils and stream sediments in Sweden. Symbol sizes and color scales for maps on the left are based on Swedish datasets, whereas those for map on the right are based on the whole European datasets.



All soil, stream, and floodplain sediment samples were prepared for analysis at the Geological Survey of the Slovak Republic. The REEs were determined in topsoils (0–25 cm depth), subsoils (the C soil horizon), and stream sediments by ICP-MS at the Geological Survey of Finland (topsoil and subsoil samples) and at the Geological Survey of France (stream and floodplain sediment samples).

#### 4.1. REE baseline levels in Sweden based on FOREGS data

In this study, we present interpolated maps of the FOREGS REE data. These maps were prepared with ArcView software, using the inverse distance weighted (IDW) algorithm to generate a regular grid. In Table 1, the basic statistics of REEs in different sample media from Europe and Sweden are compared. The geochemical data have also been interpolated through inverse distance weighting (IDW) algorithm, which preserves the information contained in point sample data. This resulted in maps portraying geochemical distribution trends that broadly match geological and other features (Cheng et al., 2001; Fedele et al., 2008; Lima et al., 2008). In general, the distribution patterns of most REEs in Sweden are similar to those in Europe. Typically, the lowest REE concentrations occur in soils and sediments overlying siliciclastic sediments (e.g., Dala sandstone in central-western Sweden) and carbonates of different age (Proterozoic to Quaternary). In contrast, high REE concentrations occur in northern Sweden (Norrbotten), northeastern Sweden (Västerbotten), central-northwestern Sweden (Jämtland), southeastern Sweden (Småland) and southwestern Sweden close to the border with Norway (Bohuslan).

The La data in Europe subsoils have a median of 25.6 mg/kg and maximum value of 155 mg/kg, with values higher than the median only over the Italian alkaline magmatic province (IAMP), in northern Portugal, and Spain (the Iberian Massif) (Fedele et al., 2008). In Sweden, La values in subsoils are lower than elsewhere in Europe (Fig. 2), with a median of 21.40 mg/kg and a maximum value of 47.10 mg/kg (Table 1). The highest La concentrations in Sweden are observed in stream sediments (up to 125 mg/kg), which have a median of 37.60 mg/kg that is higher than the median for stream sediments in Europe. The most possible sources of high La levels in soils and stream sediments are leucogranites, pegmatites, and clay-rich soils (secondary La concentrations). Migmatized bedrock with well-developed leucosome is another possible source of high La in soils and sedimentary cover.

The Ce concentrations in Europe and Sweden are similar in terms of median values. The highest values of Ce in European subsoils and topsoils are 379 mg/kg and 267 kg/mg, respectively. The median Ce values in Europe are 56.8 mg/kg and 48.2 mg/kg in topsoils and subsoils, respectively. The Ce concentrations in Swedish topsoils and subsoils have maximum values of 101 mg/kg and 83 mg/kg, respectively, with corresponding median values of 48.8 mg/kg in topsoils and 34.80 mg/kg in subsoils. The Ce concentrations in European stream sediments show maximum value of 1080 mg/kg and median of 66.6 kg/mg, whereas Ce concentrations in Swedish stream sediments show 301 mg/kg and 77.40 mg/kg for maximum and median values, respectively. Thus, Ce contents in various environmental media are quite similar in European and Swedish scales. High Ce values occur over granitic and metamorphic rocks of Northern Portugal and Spain, in IAMP, in karstic areas of Slovenia and Croatia, on the Massif Central, in SW Norway and northern Sweden. In Sweden, high Ce concentrations reflect both the type of bedrock and some mineralizations. High Ce contents (Fig. 3) in central Sweden (Dalsland and Jämtland), in Småland (SE Sweden), and Bohuslan (SW Sweden) correlate with evolved granites. The Ce anomalies in northern Sweden can be related to iron mineralizations, e.g., Kiruna type of apatite-iron deposits.

Maximum values of Pr in European vary from 32.9 mg/kg in topsoils to 125 mg/kg in stream sediments. Maximum values of Pr in European vary from 32.9 mg/kg in topsoils to 125 mg/kg in stream sediments.

The same changes in Swedish FOREGS data, from 11.40 mg/kg to 36.1 mg/kg from subsoil to stream sediment. The median value of Pr in Europe and Sweden is almost the same and ranges in median value from 6 mg/kg to 7.3 mg/kg and 5.3 mg/kg to 9.7 mg/kg in Europe and Sweden, respectively. Pr anomalies in Sweden overlap to large extent with Ce anomalies and they show highest levels in the northern part of country.

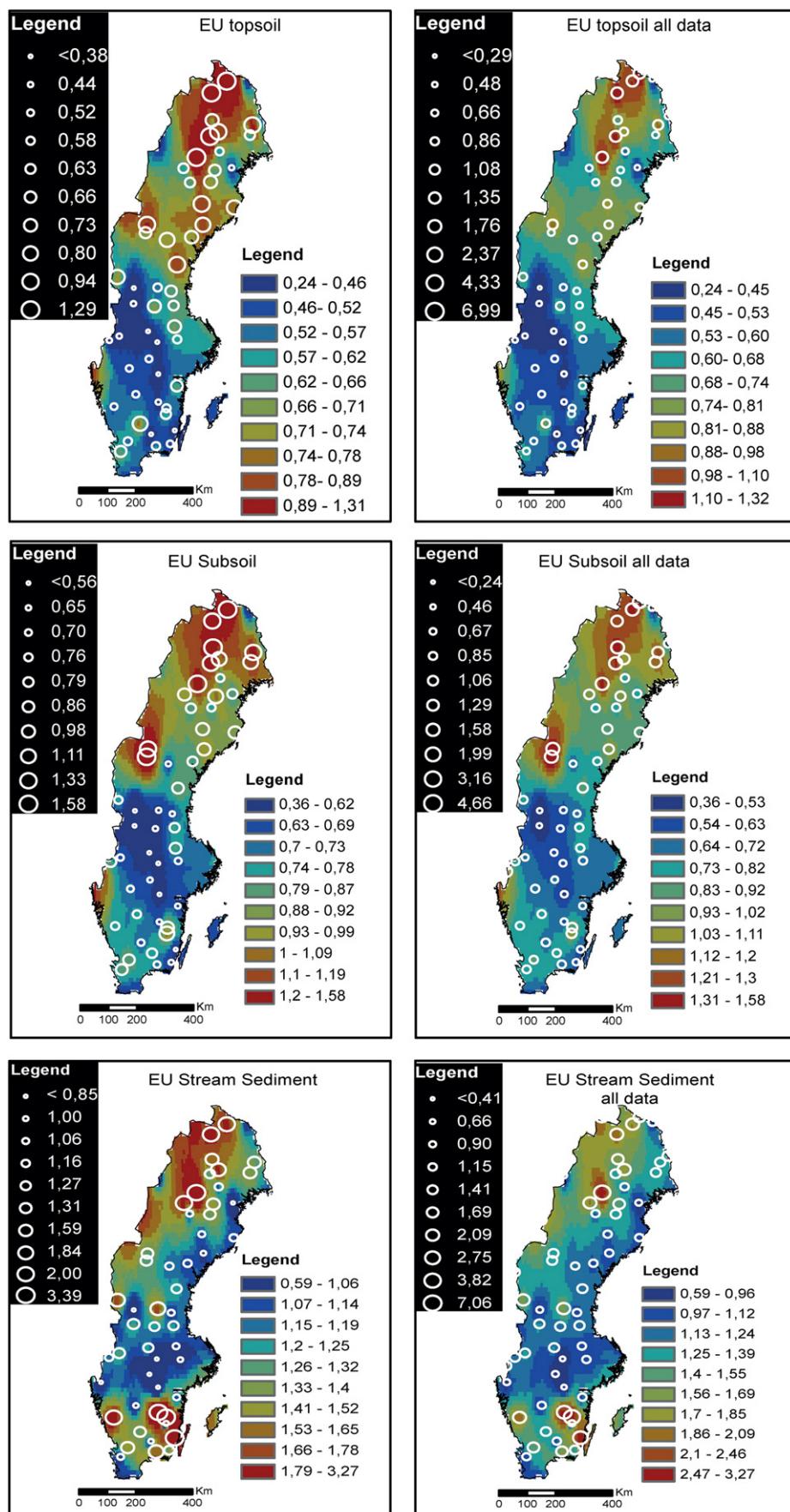
The Nd concentrations in European subsoils have a median of 22.4 mg/kg and maximum of 111 mg/kg. In Sweden, Nd values in subsoils are lower than elsewhere in Europe, with a median of 19.2 mg/kg and a maximum of 41.1 mg/kg. The highest Nd concentrations in Sweden are observed in the stream sediments (up to 139 mg/kg) with a median around 37.90 mg/kg. The Nd concentrations in Swedish topsoils are also low compared to European levels. Much lower Nd concentrations in topsoils in the southern part of Sweden may be related to the glacial deposits over crystalline bedrock of Paleoproterozoic rocks. Positive Nd anomalies point to the occurrences of crystalline rocks, while the low values in Dalarna and southern part of Sweden correlate with sedimentary rocks, e.g., Dala sandstone, Cambro-Silurian limestone and shale, and younger Mesozoic sedimentary rocks in Skåne in southern part of Sweden.

The Sm concentrations in Swedish subsoils range between 2.3 and 8.33 mg/kg, and the median of 3.80 mg/kg is slightly lower than in European subsoils (4.38 mg/kg). The Sm concentrations in Swedish topsoils range from 1.37 to 6.01 mg/kg, and the median of 2.76 mg/kg is lower than in European subsoils (3.96 mg/kg). The Sm contents in Swedish stream sediments vary from 3.49 to 24.60 mg/kg, whereas European stream sediments contain 0.2–106 mg/kg Sm. The median value of Sm in Swedish stream sediments (7.25 mg/kg) is slightly higher than that of European stream sediments (5.4 mg/kg). Locally, Sm contents are high in stream sediments in northern parts of Europe. Generally, values of Sm over Europe are quite low (<10 mg/kg) and Sm anomalies follow the pattern observed for Nd (Fedele et al., 2008).

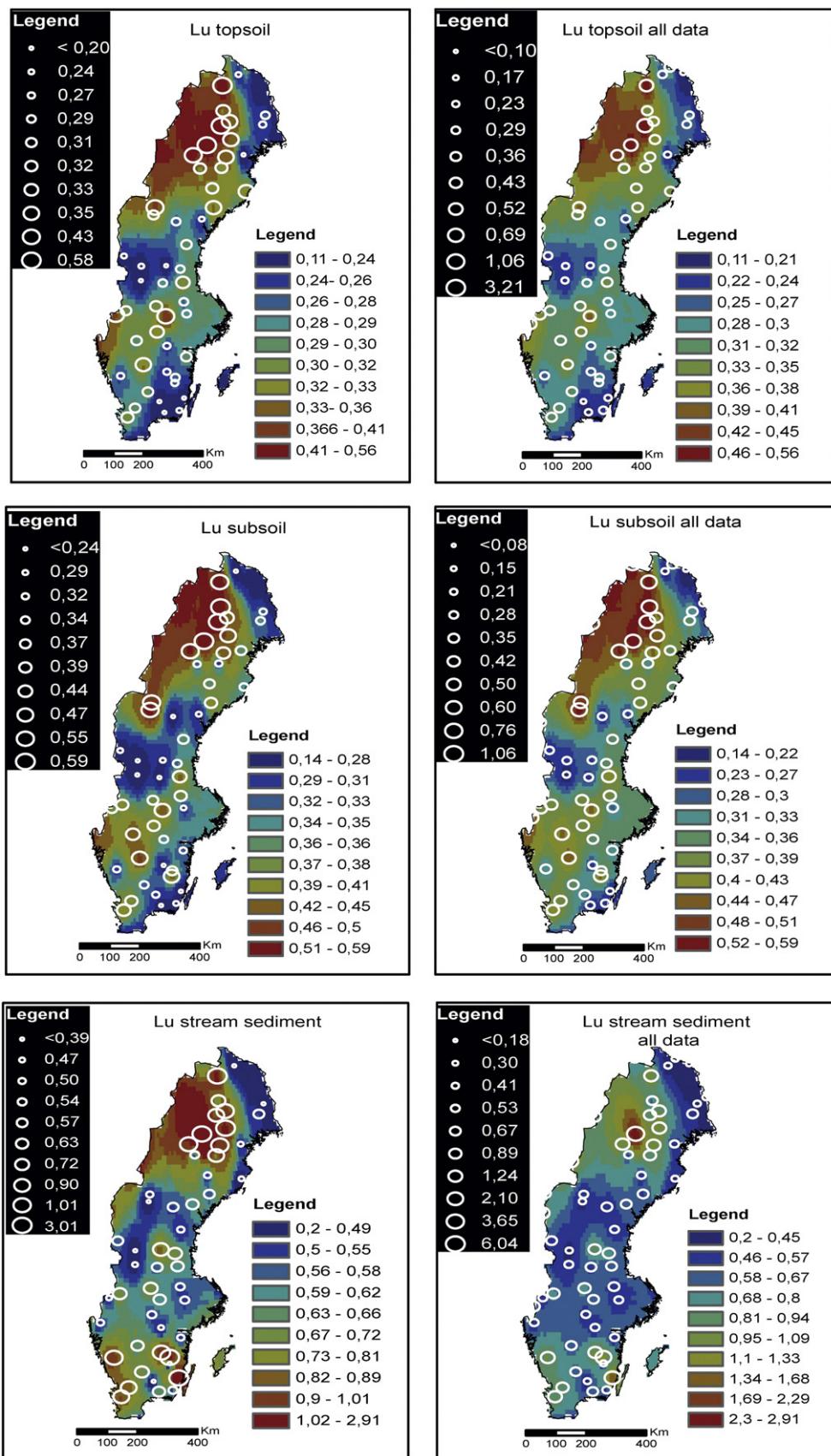
In Swedish subsoils, Eu contents range from 0.36 to 1.58 mg/kg and the median is 0.78 mg/kg. In Europe subsoils, Eu contents range from 0.05 to 4.66 mg/kg and the median is 0.84 mg/kg. Concentrations of Eu in Swedish topsoils vary from 0.24 to 1.29 mg/kg with a median of 0.63 mg/kg. In contrast, concentrations of Eu in European topsoils vary from 0.05 to 6.99 mg/kg with a median of 0.77 mg/kg. In Swedish stream sediments, Eu values range between 0.57 and 3.39 mg/kg, and the median is 1.25 mg/kg. The highest Eu concentrations occur in northern Sweden where soils overlie Archean and Paleoproterozoic basement rocks, in central Jämtland, Västerbotten, and in Bohuslan where soils are underlain by younger evolved granitoids (Fig. 4).

European subsoils have a median Gd concentration of 4.24 mg/kg and a maximum Gd value of 16 mg/kg. Swedish subsoils have Gd values of 2.25 to 7.89 mg/kg with a median of 3.82 mg/kg. Swedish topsoils have Gd contents of 1.15 to 6.40 mg/kg, with median of 2.89 mg/kg. This is slightly less than median Gd content of European topsoils (3.85 mg/kg). The highest Gd concentrations in Sweden are observed in the stream sediments (up to 26.80 mg/kg) with a median of 7.31 mg/kg. The areas with high Gd concentrations in Sweden overlap with Eu anomalies. In northern Sweden, high Gd contents correlate with Palaeoproterozoic granite and pegmatite; whereas in the southern part of Sweden, high Gd contents correlate with occurrences of post-orogenic granites within the Fennoscandian Shield and young Neoproterozoic granitoids (ca. 900 Ma old) in Bohuslan.

The Tb values in Swedish subsoils vary between 0.36 and 1.17 mg/kg, and the median is 0.61 mg/kg. In Swedish topsoils, Tb contents vary from 0.22 to 1.08 mg/kg and the median is 0.47 mg/kg. The median Tb values in European topsoils and subsoils are almost the same as those in Sweden. In stream sediments, Tb contents range from 0.65 to 4.26 mg/kg and the median is 1.03 mg/kg. This is slightly higher than the median Tb value in European stream sediments (0.79 mg/kg). The higher concentrations of



**Fig. 4.** Geochemical maps of Eu in topsoils, subsoils and stream sediments in Sweden. Symbol sizes and color scales for maps on the left are based on Swedish datasets, whereas those for map on the right are based on the whole European datasets.



**Fig. 5.** Geochemical maps of Lu in topsoils, subsoils and stream sediments in Sweden. Symbol sizes and color scales for maps on the left are based on Swedish datasets, whereas those for map on the right are based on the whole European datasets.

**Table 2**

Pearson correlation matrices for the topsoil, subsoil and stream sediment REE data. Values greater than 0.90 are indicated in bold.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
<i>Topsoils (n = 51)</i>														
La	1.00													
Ce	<b>0.93</b>	1.00												
Pr	<b>0.99</b>	<b>0.90</b>	1.00											
Nd	<b>0.98</b>	<b>0.90</b>	<b>0.99</b>	1.00										
Sm	<b>0.94</b>	0.86	<b>0.97</b>	<b>0.98</b>	1.00									
Eu	0.83	0.77	0.85	0.89	0.88	1.00								
Gd	0.88	0.82	<b>0.92</b>	<b>0.94</b>	<b>0.97</b>	0.89	1.00							
Tb	0.83	0.77	0.87	<b>0.91</b>	<b>0.94</b>	0.87	<b>0.98</b>	1.00						
Dy	0.75	0.70	0.79	0.83	0.87	0.83	<b>0.93</b>	<b>0.97</b>	1.00					
Ho	0.69	0.64	0.73	0.78	0.82	0.81	<b>0.90</b>	<b>0.94</b>	<b>0.97</b>	1.00				
Er	0.65	0.61	0.68	0.73	0.77	0.77	0.86	<b>0.91</b>	<b>0.95</b>	<b>0.98</b>	1.00			
Tm	0.58	0.54	0.63	0.67	0.71	0.70	0.82	0.86	<b>0.92</b>	<b>0.96</b>	<b>0.96</b>	1.00		
Yb	0.55	0.53	0.58	0.64	0.67	0.69	0.79	0.84	<b>0.90</b>	<b>0.95</b>	<b>0.96</b>	<b>0.97</b>	1.00	
Lu	0.45	0.45	0.49	0.54	0.57	0.60	0.70	0.76	0.85	<b>0.91</b>	<b>0.93</b>	<b>0.96</b>	<b>0.96</b>	1.00
<i>Subsoils (n = 51)</i>														
La	1.00													
Ce	<b>0.95</b>	1.00												
Pr	<b>0.98</b>	<b>0.95</b>	1.00											
Nd	<b>0.97</b>	<b>0.92</b>	<b>0.99</b>	1.00										
Sm	<b>0.92</b>	0.89	<b>0.96</b>	<b>0.98</b>	1.00									
Eu	0.85	0.79	0.89	<b>0.90</b>	<b>0.90</b>	1.00								
Gd	0.86	0.84	<b>0.91</b>	<b>0.93</b>	<b>0.97</b>	0.88	1.00							
Tb	0.82	0.81	0.89	<b>0.91</b>	<b>0.96</b>	0.86	<b>0.98</b>	1.00						
Dy	0.71	0.71	0.79	0.82	0.89	0.78	<b>0.93</b>	<b>0.97</b>	1.00					
Ho	0.67	0.66	0.74	0.77	0.85	0.76	<b>0.90</b>	<b>0.94</b>	<b>0.98</b>	1.00				
Er	0.60	0.59	0.68	0.72	0.80	0.69	0.85	<b>0.90</b>	<b>0.95</b>	<b>0.97</b>	1.00			
Tm	0.58	0.58	0.67	0.70	0.79	0.70	0.85	0.89	<b>0.94</b>	<b>0.96</b>	<b>0.97</b>	1.00		
Yb	0.55	0.55	0.63	0.67	0.76	0.65	0.81	0.88	<b>0.92</b>	<b>0.96</b>	<b>0.97</b>	<b>0.97</b>	1.00	
Lu	0.51	0.51	0.58	0.62	0.70	0.63	0.76	0.83	<b>0.90</b>	<b>0.93</b>	<b>0.94</b>	<b>0.94</b>	<b>0.95</b>	1.00
<i>Stream sediments (n = 51)</i>														
La	1.00													
Ce	<b>0.97</b>	1.00												
Pr	<b>0.99</b>	<b>0.96</b>	1.00											
Nd	<b>0.98</b>	<b>0.94</b>	<b>1.00</b>	1.00										
Sm	<b>0.94</b>	0.89	<b>0.97</b>	<b>0.99</b>	1.00									
Eu	0.87	0.81	<b>0.90</b>	<b>0.92</b>	<b>0.92</b>	1.00								
Gd	0.90	0.83	<b>0.94</b>	<b>0.96</b>	<b>0.99</b>	<b>0.90</b>	1.00							
Tb	0.84	0.76	0.89	<b>0.92</b>	<b>0.96</b>	0.88	<b>0.99</b>	1.00						
Dy	0.76	0.66	0.81	0.85	<b>0.91</b>	0.84	<b>0.96</b>	<b>0.99</b>	1.00					
Ho	0.72	0.62	0.78	0.82	0.89	0.81	<b>0.94</b>	<b>0.97</b>	<b>0.99</b>	1.00				
Er	0.68	0.57	0.74	0.78	0.85	0.77	<b>0.91</b>	<b>0.96</b>	<b>0.99</b>	<b>1.00</b>	1.00			
Tm	0.64	0.53	0.70	0.74	0.82	0.75	0.89	<b>0.94</b>	<b>0.97</b>	<b>0.99</b>	<b>1.00</b>	1.00		
Yb	0.60	0.48	0.66	0.70	0.79	0.73	0.86	<b>0.91</b>	<b>0.96</b>	<b>0.98</b>	<b>0.99</b>	<b>1.00</b>	1.00	
Lu	0.59	0.47	0.65	0.69	0.78	0.71	0.85	<b>0.91</b>	<b>0.95</b>	<b>0.97</b>	<b>0.98</b>	<b>0.99</b>	<b>0.99</b>	1.00

Tb are found in regions with igneous rocks, mostly granitic to pegmatitic in composition. In the southern part of Sweden, some anomalies may relate to the glacial deposits overlying crystalline bedrock.

The median for Dy is 3.55 mg/kg in subsoil and range vary from 2.02 mg/kg to 7.23 mg/kg. In topsoil the median Dy value is 2.94 mg/kg; content in topsoil vary from 1.48 mg/kg to 6.18 mg/kg, while the median Dy at Europe is 3.66 mg/kg and 3.42 mg/kg in subsoil and topsoil, respectively. The median Dy content in stream sediment is 5.78 mg/kg and the range of concentrations varies between 3.78 mg/kg and 25.30 mg/kg. Dy concentrations in soil are much higher in northern Sweden than in the south. High Dy values in soil are located mainly in the crystalline basement and loess/paleoplacer area of northern Sweden. Dy pattern in subsoil and topsoil is very similar. High Dy values also occur in stream sediment in the northern part of Sweden and mostly have a good correlation with Th and U.

The Ho contents of Swedish subsoils range from 0.37 to 1.47 mg/kg with a median of 0.75 mg/kg, which is similar to the median Ho content of European subsoils. The values of Ho in Swedish topsoils are similar to those of the subsoils and the highest Ho concentrations are found in areas with crystalline basement rocks in northern Sweden. Concentrations of Ho in soils have strong correlations with concentrations of Gd, Tb, and Dy. The median Ho value in Swedish

stream sediments is 1.20 mg/kg, which is slightly higher than the median Ho value in European stream sediments. Anomalies of Ho occur in northern and southern parts of Sweden, where they are related to granitic–pegmatitic lithologies enriched in U and Th.

The Er concentrations in Swedish subsoils range from 1.21 to 4.39 mg/kg with median of 2.24 mg/kg, whereas Er contents of topsoils very from 0.95 to 3.96 mg/kg with a median of 1.80 mg/kg. The Er contents of Swedish stream sediments vary from 2.14 to 17.30 mg/kg with a median of 3.47 mg/kg, whereas the median Er value in European sediments is 2.67 mg/kg. The Er median in Swedish stream sediments is higher than that in Swedish soils (3.47 mg/kg). High Er values in Swedish soils are found mainly on the crystalline basement with granitic composition and in paleoplacer areas in northern Sweden (Salpeteur et al., 2005). The distribution of Er anomalies in Sweden is similar to that of heavy REE elements.

The Tm contents of Swedish subsoils vary from 0.17 to 0.65 mg/kg with median of 0.36 mg/kg, whereas in Swedish topsoils Tm values vary from 0.13 to 0.57 mg/kg with median of 0.28 mg/kg. The spatial distribution of Tm is very similar to other heavy REEs and controlled mainly by the crystalline bedrock underlying the soils. The median Tm value in Swedish stream sediment is 0.53 mg/kg, which is slightly higher than that of European stream sediments. A reason for this is

the strong correlation of REEs with U and Th in granite–pegmatite rocks and felsic volcanics in the northern part of Sweden.

The spatial distribution of Yb is similar to that of Tm and Er, but areas with elevated values of these elements are generally smaller. The median Yb values in Swedish subsoils and topsoils are 2.40 mg/kg and 1.98 mg/kg, respectively. The concentrations of Yb in stream sediments, which range from 2.26 to 18.70 mg/kg with a median of 3.76 mg/kg, are higher than in the soils. High Yb values in soils are located mainly in regions underlain by the crystalline basement of mainly granitic composition and in areas with high-grade metamorphic rocks (amphibolites, migmatites, granulites, and eclogites) with garnet is a common phase. Paleoplae area in northern Sweden tends to have higher Yb concentrations as well (Salpeteur et al., 2005). There are strong correlations of Yb with U and Th in stream sediments, possibly because these elements form substitutions in heavy minerals commonly found in stream sediments (e.g., garnet).

The Lu values in Swedish subsoils range from 0.18 to 0.59 mg/kg with median of 0.35 mg/kg, whereas Lu values in topsoils vary between 0.17 and 0.58 mg/kg with median of 0.30 mg/kg (Fig. 5) The median Lu values in Swedish subsoils and topsoils are almost similar to those in European subsoils/topsoils. Low Lu concentrations in Swedish soil occur in areas with metavolcanic rocks and younger granitoids in central and northern Sweden. High Lu contents have been noted in the Paleoproterozoic granite–pegmatite series in northern and southeastern Sweden. The Lu contents of Swedish stream sediments range from 0.34 to 3.01 mg/kg with a median of 0.57 mg/kg, which is higher than for European stream sediments (0.39 mg/kg). The spatial distribution of Lu in stream sediments shows similar trends to the other media and there are strong correlations among Lu, Yb, and Tm.

#### 4.2. Principal component analysis of REE data

Principal component (PC) analysis has been a conventional multivariate technique that is used for studying geochemical data (Carranza, 2008; Howarth and Sinding-Larsen, 1983). PC analysis reduces a large number of variables to a smaller number, allowing the user to determine which components (groups of variables) account for variation in multivariate data (Güller et al., 2002). PC analysis has been applied frequently to process and interpret geochemical and other types of spatial data (e.g., Carranza, 2008; Cheng et al., 2011; Grunsky, 2010; Harris et al., 1997). PC analysis has also been used in GIS for integration and interpretation of image data (e.g., Carranza and Hale, 2002; Chavez and Kwarteng, 1989; Crósta et al., 1989). The foundation of PC analysis is the correlation (covariance) matrix, which measures the interrelationships among multiple variables. The first PC explains most of the variance within the original data, and each subsequent PC explains progressively less of the variance. A multivariate dataset can usually be reduced to two or three PCs that account for the majority of the variance within the dataset.

Pearson correlation analysis was performed on the FOREGS REE data for the individual sampling media (Table 2). The results show strong correlations among LREEs (e.g., La with Ce, Pr, and Sm) in all media. The results also show strong correlations among HREEs (e.g., Er with Lu, Yb, and Tm).

Subsequently, PC analysis was performed on the average values of the different sampling media. The results reported in Table 3 show that PC1 and PC2 explain 82.60% and 12.77%, respectively, of the total variance in topsoils. For subsoils, PC1 and PC2 explain 83.72% and 12.11%, respectively, of the total variance in the data. For stream sediments, PC1 and PC2 explain 86.46% and 11.68%, respectively, of the total variance in the data. All REEs have negative loadings on PC1 of data for individual sampling media (Table 3). The LREEs have largest loadings on PC2 of data for individual sampling media. For data of each sampling media, Ce has largest loading on PC3 whereas Eu and Yb have negative loading on this component.

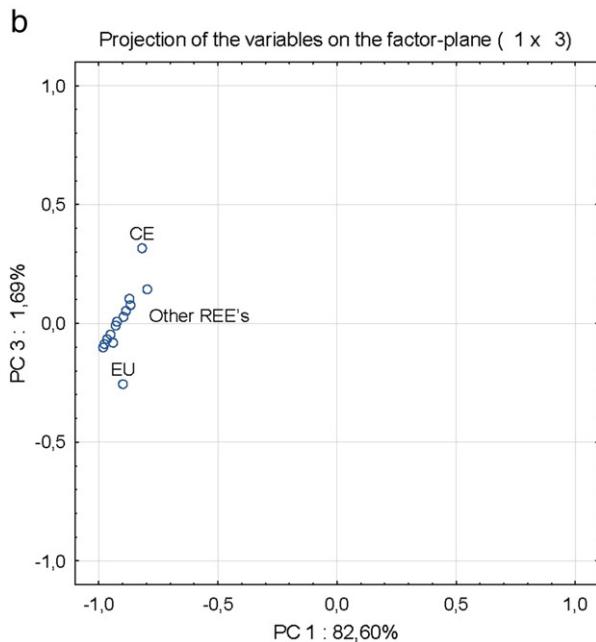
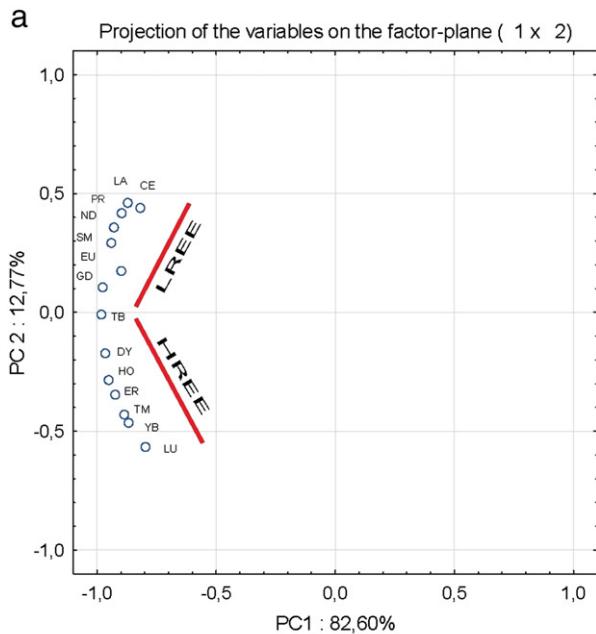
The datasets for the individual sampling media show similar multivariate structures. The PC1 and PC2 of the individual datasets show the contrast between LREEs and HREEs, whereas the PC1 and PC3 of the individual datasets show three distinct clusters (one comprising most REEs, one for Ce and one for Eu) (Figs. 6–8). Plots of loadings of REEs on PC2 and PC3 of individual datasets show mainly two distinct clusters (Fig. 9), one comprising most REEs and the other represent Eu anomalies. However, Ce forms a distinct cluster in the subsoil and topsoil datasets. This indicates that Ce in topsoils and subsoils are closely related probably in origin and dispersion. The result for stream sediment is slightly different from subsoil and topsoil, which may relate to the origin for each elements and any other weathering or mineralization.

#### 5. Discussion

The geochemical maps of REE distribution in Sweden show the possible sources of metals in relation to the type of the underlying rock

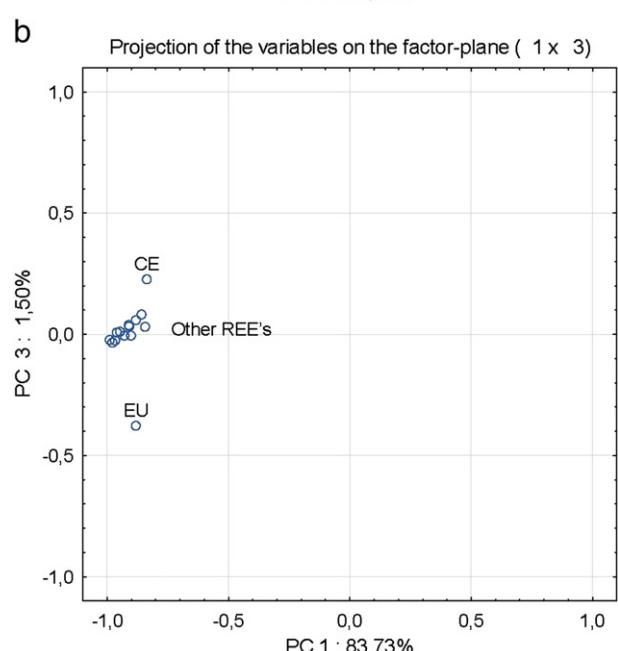
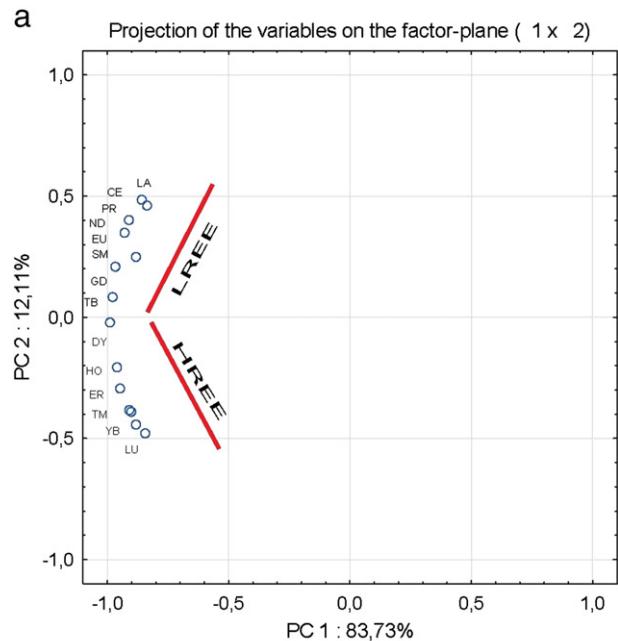
**Table 3**  
Correlations among elements and principal components.

Elements	PC1	PC2	PC3	PC4
<i>Topsoils</i>				
La	−0.075	0.258	0.439	0.048
Ce	−0.071	0.245	1.330	−0.738
Pr	−0.078	0.234	0.113	0.348
Nd	−0.080	0.199	−0.038	0.083
Sm	−0.081	0.164	−0.346	0.757
Eu	−0.078	0.097	−1.075	−1.959
Gd	−0.084	0.059	−0.364	0.531
Tb	−0.085	−0.005	−0.430	0.641
Dy	−0.083	−0.096	−0.285	0.424
Ho	−0.082	−0.159	−0.199	0.180
Er	−0.079	−0.194	0.033	−0.011
Tm	−0.077	−0.241	0.226	0.102
Yb	−0.075	−0.260	0.324	−0.396
Lu	−0.069	−0.317	0.606	−0.311
Eigenvalue	11.565	1.788	0.237	0.159
Cumulative variance (%)	82.605	95.377	97.071	98.213
<i>Subsoils</i>				
La	−0.858	0.485	0.081	−0.088
Ce	−0.837	0.460	0.228	−0.084
Pr	−0.910	0.401	0.039	−0.026
Nd	−0.929	0.349	−0.005	0.024
Sm	−0.967	0.208	−0.026	0.089
Eu	−0.882	0.249	−0.377	−0.112
Gd	−0.977	0.083	−0.034	0.144
Tb	−0.989	−0.022	−0.023	0.107
Dy	−0.960	−0.207	0.008	0.106
Ho	−0.946	−0.294	0.011	0.026
Er	−0.909	−0.383	0.033	0.009
Tm	−0.902	−0.391	−0.006	−0.026
Yb	−0.882	−0.442	0.059	−0.042
Lu	−0.845	−0.479	0.031	−0.185
Eigenvalue	11.723	1.696	0.209	0.118
Cumulative variance (%)	83.734	95.849	97.349	98.196
<i>Stream sediments</i>				
La	−0.880	0.458	0.052	0.059
Ce	−0.804	0.571	0.106	0.095
Pr	−0.920	0.387	0.031	0.009
Nd	−0.942	0.331	0.015	−0.018
Sm	−0.976	0.195	0.013	−0.073
Eu	−0.907	0.207	−0.367	0.022
Gd	−0.992	0.063	0.041	−0.091
Tb	−0.994	−0.062	0.021	−0.083
Dy	−0.974	−0.209	0.005	−0.070
Ho	−0.961	−0.267	0.027	−0.019
Er	−0.941	−0.333	0.029	0.008
Tm	−0.921	−0.385	0.015	0.049
Yb	−0.899	−0.432	−0.004	0.061
Lu	−0.891	−0.438	0.016	0.093
Eigenvalue	12.108	1.636	0.154	0.154
Cumulative variance (%)	86.485	98.174	99.274	99.661



**Fig. 6.** Principal component analysis of Swedish topsoil dataset. Correlations of elements with PCs: (a) PC1 versus PC2; (b) PC1 versus PC3.

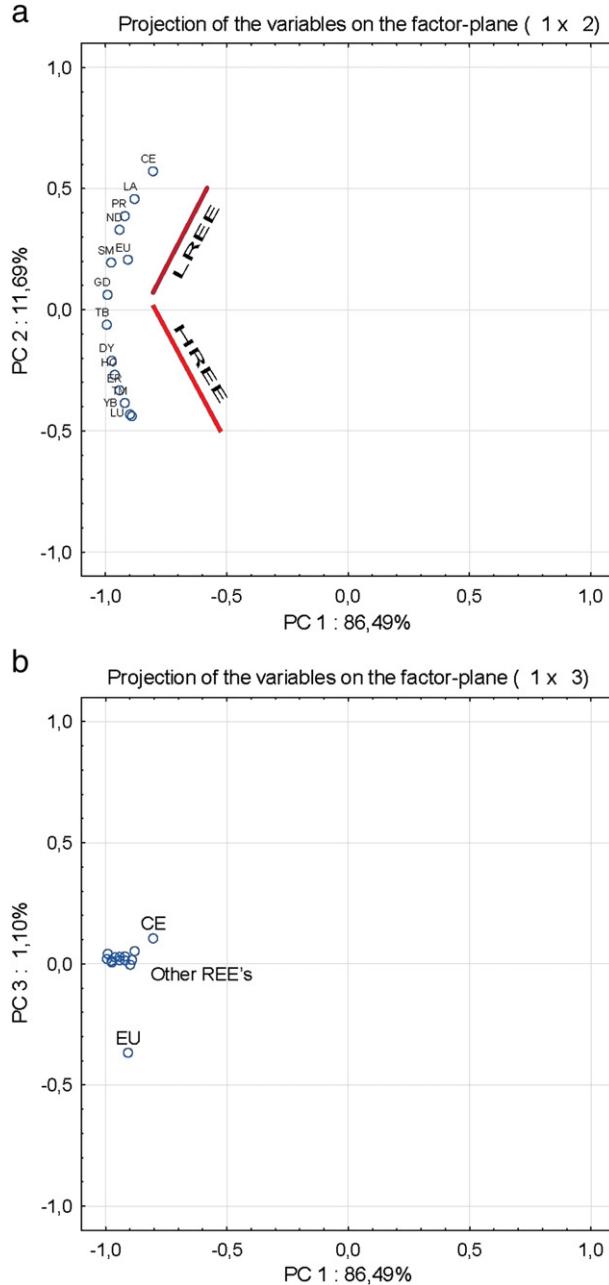
types. In northern Sweden, the large REE anomaly probably has a complex origin; the high REE concentrations correlate with underlying crystalline rocks of the Fennoscandian Shield, and granitic intrusions and high grade metamorphic rocks within the Caledonides. Another potential source of REEs is hydrothermally altered igneous and metavolcanic rocks, which host important ore deposits (Fe, Cu, Zn etc). The high REE concentrations in Jämtland in west northern part of Sweden at Caledonian region originate from granites of the autochthonous basement rocks (the Grong-Olden Culmination) which form a tectonic window within the Caledonides. In addition to the REEs, these lithologies are known to host uranium mineralization. Higher REE concentrations close to the Baltic coast in central Sweden can be related to the high-grade migmatites and large igneous intrusions (e.g., Ljusdal Batholith). In southern Sweden, the high REEs are related to evolved post-orogenic granites and pegmatites of Svecokarelian (SE Sweden) and Sveconorwegian (SW Sweden) age.



**Fig. 7.** Principal component analysis of Swedish subsoil dataset. Correlations of elements with PCs: (a) PC1 versus PC2; (b) PC1 versus PC3.

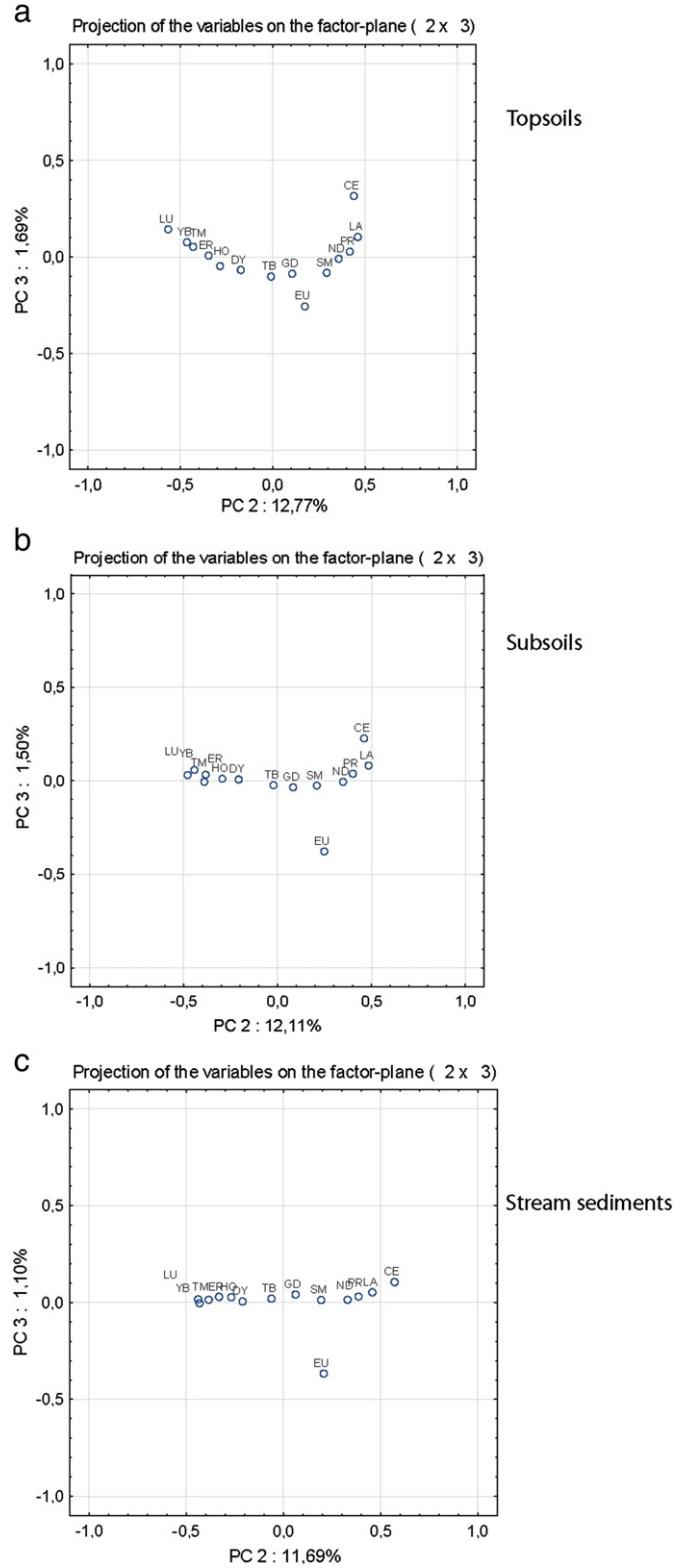
The geochemical maps and correlation matrices show a general decoupling between LREE and HREE. The main reason for this difference is that the LREE are highly incompatible in the magmatic and metamorphic environments, which dominate Swedish bedrock geology, while HREE are somewhat more compatible. The LREEs concentrate in highly evolved rocks and the final products of magma differentiation (accessory minerals), while HREE tend to substitute for major elements in some rock forming and metamorphic minerals (e.g., clinopyroxene and garnet).

The median concentration of REE followed the order Ce > La > Nd > Pr > Sm > Gd > Dy > Er > Yb > Eu > Ho > Tb > Tm > Lu in subsoils, Ce > La > Nd > Pr > Sm > Gd > Dy > Yb > Er > Eu > Ho > Tb > Tm > Lu in topsoils, and Ce > La > Nd > Pr > Sm > Gd > Dy > Er > Yb > Ho > Tb > Eu > Lu > Tm in stream sediments. The REE patterns are generally similar by having higher LREE concentrations, a slightly negative Eu anomaly and depletion in HREE concentrations in all media. The



**Fig. 8.** Principal component analysis of Swedish stream sediment dataset. Correlations of elements with PCs: (a) PC1 versus PC2; (b) PC1 versus PC3.

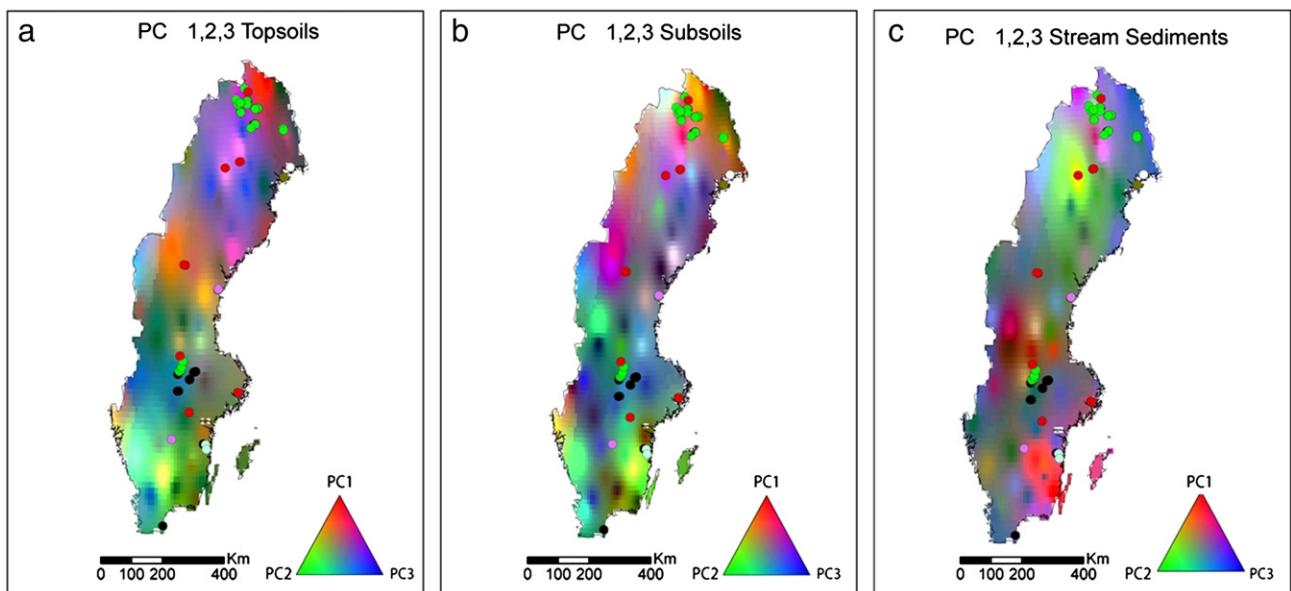
main difference between the distribution pattern for LREE and HREE is the enrichment of the LREE in Archean rocks in northern Sweden while HREE concentrations in the oldest rocks and located southeastwards (along the border with Finland) Archean to Paleoproterozoic metasediments are rather low. Enrichment of HREE in southern Sweden occurs in soils overlying high grade metamorphic rocks of the Sveconorwegian terrane. High-grade rocks (garnet migmatites, granulites, and eclogites) are responsible for elevated Yb and Lu contents in the Middle and Upper Allochthons in the Caledonides (e.g., in the Seve Nappe). The main REE negative anomaly occurs in Dalarna (central Sweden) where Mesoproterozoic quartzitic sandstone exhibits quartz-dominated, strongly depleted composition. Soils overlying Cambro-Silurian sedimentary rocks (shale, limestone, marl etc) in central and southern Sweden, Gotland, and Öland also have low REE concentrations. Skåne in southernmost Sweden with the youngest



**Fig. 9.** Principal component analysis of individual Swedish datasets. Correlations of elements with PC2 and PC3: (a) topsoils; (b) subsoils; and (c) stream sediments.

sedimentary cover in Sweden, closely related to the continental Europe, shows low REE concentrations in all sample types.

In nature, the REEs generally act together. Therefore, multivariate methodologies can be applied to this series of elements to identify and examine anomalies. PC analysis aids interpretation of geochemical data in terms of geological process, such as differentiation (partial



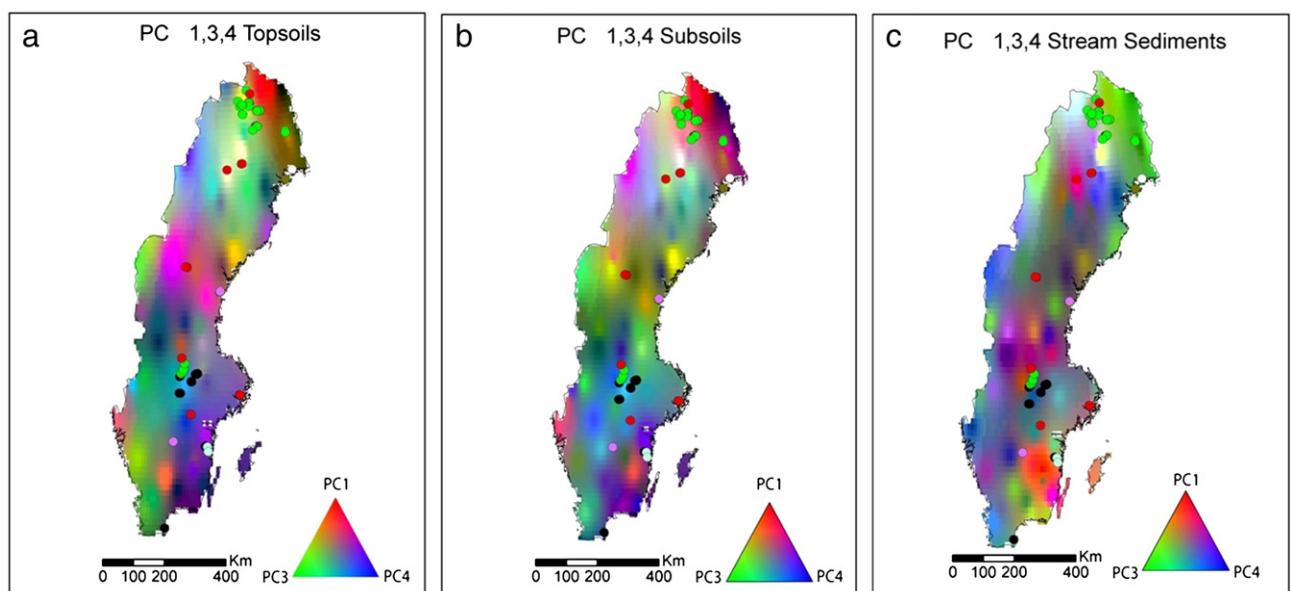
**Fig. 10.** Color composite images of PC1 (red), PC2 (green) and PC3 (blue) of individual Swedish datasets: (a) topsoils; (b) subsoils; (c) stream sediments. For explanations of colored dots, see Fig. 1.

melting, crystal fractionation, etc.), alteration/mineralization, and weathering (Grunsky, 2010). The first and second PCs usually reveal relationships between observations and variables that reflect underlying lithological variation. In Sweden, where a significant percentage of the surface is covered with overburden such as glacial till, alluvium, or colluvium, the combination of variables and plots of PC loadings reflect a mixture of several surficial processes.

The first two PCs of each of the topsoil and subsoil REE soil datasets account for 95.37% and 95.84%, respectively, of the total variance in each of those datasets. The projections of the 14 REEs on the bi-dimensional space (Figs. 5–7) show the degree of association among the variables. Both LREEs and HREEs form well-defined groups. The Ce plots away from the other REEs due to its anomalous nature. The Eu also plots away from the LREE group due to its distinct behavior among the REEs. Of all the REEs, Ce and Eu show different distribution patterns,

possibly due to the sensitivity of the REEs to redox conditions as shown by Henderson (1984) and Wilde et al. (1996).

The color composite maps of PCs 1, 2 and 3 of the topsoil and subsoil data (Fig. 10) clearly reflect the Archean rocks in northern Sweden and the outline of the second phase of the Svecokarelian orogen, as well as the clay belt along the coast in eastern Sweden and young granites in the southwest. Some mineralizations in northern Sweden are clearly marked on the PCs maps. It is also interesting that different types of REE mineralization are associated with different PC scores (i.e., different colors in the PC color composites). In Fig. 11, which is a color composite map of PC 1, 3 and 4, more details on the variation of PCs related to mineralization can be observed. In this work, color composites of the first three to fourth PCs of each dataset are effective for interpretation of the geochemical data in terms of geological processes.



**Fig. 11.** Color composite images of PC1 (red), PC3 (green) and PC4 (blue) of individual Swedish datasets: (a) topsoils; (b) subsoils; (c) stream sediments. For explanations of colored dots, see Fig. 1.

## 6. Conclusion

Principal component analyses of rare earth element concentration data in the FOREGS datasets for subsoils, topsoil and stream sediments in Sweden show that each of these datasets comprises three main components from which meaningful interpretations regarding REE distribution in Swedish soils can be drawn. There are strong correlations among REEs in soils and in the underlying bedrock. In topsoils, the highest REE concentrations develop over Archean granites and along the boundary of Archean and Palaeoproterozoic rocks whereas the lowest REE concentrations pertain to soils derived from Sveconorwegian orogen rocks. Subsoils shows slightly different REE distributions, with the highest concentrations developed on Caledonian and Svecokarelian orogen (phase 2) rocks. The highest REE concentrations in stream sediments are generally similar to those in subsoils, but the anomalies also show the boundary of Archean and Palaeoproterozoic rocks in northern Sweden. The lowest REE concentrations occur in soils overlying siliciclastic and carbonate rocks of various ages. LREEs show strong enrichment over HREEs in soils overlying the Archean rocks in northern Sweden, Archean and Palaeoproterozoic basement rocks in Jämtland and Västerbotten, and younger granites in Bohuslan. In contrast, the HREEs show strong enrichment in soils overlying high-grade metamorphic rocks of the Sveconorwegian Orogen in southern Sweden. REE data for stream sediments show various subtle distribution patterns compared to those for subsoils and topsoils. This is attributed to different styles of sediment re-working as well as weathering and biogeochemical processes that the sediments have undergone.

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## **REE contents in solid sample media and stream water from different geological contexts: Comparison between Italy and Sweden**

### ***Sammanfattning av artikel 3***

Artikeln baseras på FOREGS data från fem provmedia. Analysresultat för sällsynta jordartsmetaller i ytlig jord (topsoil) och dess underlag (subsoil), älvsediment (stream sediment) och översvämningssediment (flood plain) samt strömmande vatten har jämförts mellan Italien och Sverige med avseende på koncentrationerna av sällsynta jordartsmetaller och på skillnader i klimat, berggrundsgeologi och bildning av jord. Geologin i Italien och Sverige har beskrivits i ett inledande avsnitt för respektive land för klargöra variationer i koncentrationerna av vissa sällsynta jordartsmetaller i relation till berggrundsgeologin. Grundläggande statistiska parametrar för sällsynta jordartsmetaller i fem medier finns i tabellform för de två länderna. Därtill har interpolerade kartor tagits fram för alla medier, och de viktigaste koncentrationerna och anomalierna har beskrivits.

En utförlig tabell beskriver fördelningen av och förekomster med sällsynta jordartsmetaller i de undersökta provmedierna för Italien och Sverige. Principalkomponentanalys (PCA) har tillämpats baserat på ett liknande sätt som i artikel 2, och likheter och skillnader i PCA-data har förklarats för respektive land. Baserat på PCA kan viss anrikning av sällsynta jordartsmetaller i Sverige kopplas till mineralisering, och viss anrikning av sällsynta jordartsmetaller i marken i Italien knytas till användningen av gödningsmedel.

I Sverige och Italien kan koncentrationer av sällsynta jordartsmetaller i marken med ursprung från berggrund och jordutveckling lokalt ha ett tillskott från gödningsmedel. Innehåll av alkaligranit liksom lerigt material i marken i östra delen av Sverige (central-skandinaviska lerbältet) ger höga koncentrationer av sällsynta jordartsmetaller, medan höga koncentrationer av sällsynta jordartsmetaller i jord i Italien är kopplade till områden med vulkaniska bergarter. Sammanfattningsvis är det flera faktorer som styr innehållet av sällsynta jordartsmetaller i marken: bergart, mineralisering, typ av jord och förekomst av morän, och även vittring och klimat.

### ***Summary of Paper 3***

FOREGS data on five media (topsoil, subsoil, floodplain sediment, stream sediment and stream water) have been compared between Italy and Sweden with focus on the concentration of rare earth elements and differences in bedrock geology, soil development and climate. The geology of Italy and Sweden were described to introduce a background for understanding how some REE anomalies are related to the bedrock. Basic statistic parameters for REE data in five media are presented in a table for the two countries. In addition, interpolated maps have been produced for all media and the main concentrations and anomalies have been described.

A comprehensive table shows the distribution and occurrences of rare earth elements in the investigated media for Italy and Sweden. Principal component analysis (PCA) has been applied based on a similar concept as in paper 2 and the similarity and differences in PCA data have been explained for each country. Based on PCA, some enrichments of rare earth elements in Sweden could be recognised as caused by mineralisation and some enrichments of rare earth elements in soil in Italy could be associated with the use of fertiliser.

In Sweden and Italy, REE content inherited from bedrock and soil development can locally be affected by the use of fertiliser. The clay-rich material in the eastern part of Sweden (central Scandinavian clay belt) shows higher concentration of rare earth elements, as do alkali granites, while higher concentrations of rare earth elements in soil in Italy are commonly attributed to volcanic rocks. In summary, several factors control the REE contents in soil: rock type, mineralisation, type of soil and presence of till, weathering and climate.

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## REE contents in solid sample media and stream water from different geological contexts: Comparison between Italy and Sweden

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### ABSTRACT

Rare earth elements (REEs) are quickly gaining more and more relevance as important chemical resources due to the large number of technical applications, and as a consequence, scientific interest on REE-bearing minerals is increasing. In this work, REE data from the FOREGS Geochemical Atlas of Europe database on solid sample media (topsoil, subsoil, stream sediment, and floodplain) and stream water for Italy and Sweden are used to plot distribution maps, and Principal Component Analysis to identify patterns within the data set. The careful investigation of the spatial distribution of REEs in all sample media for both countries allowed us to identify the prominent role played by the geogenic component. Despite a similar REE content of bedrocks (alkaline igneous products, both intrusive and effusive in Italy, alkali granites and pegmatites in Sweden), several distinct differences emerged between the two countries. We identified factors like climate, geomorphology, age of deposits, presence of mineralisation, types of soil and presence of till, as responsible for the different REE enrichments in solid and aqueous sample media in the two countries. Italian palaeosols, developed in volcanic areas, were identified as a possible future source for REE extraction using low pollutant extraction techniques.

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### 1. Introduction

Since the end of last century, geochemical research has been concerned with the identification of the effects of single chemical elements on human health, and many efforts were devoted to the assessment of natural background values and to the plotting of reliable geochemical maps for main solid and aqueous sample media. In 1996, the Forum of European Geological Surveys (FOREGS) decided to compile a large database of geochemical data covering different environmental media (soil, stream and floodplain sediments and water) from 26 European countries, with the purpose of compiling the geochemical atlas of Europe (Plant et al., 1996, 1997). The collected data were described in two volumes by Salminen et al. (2005) and De Vos et al. (2006), and are freely available (<http://weppi.gtk.fi/publ/foregsatlas/>) for further investigation by all interested researchers.

While this project was being completed, rare earth elements (REEs) gained more relevance for industrial and commercial purposes, due to their increasing use in medicine as a contrast medium (Gd), in advanced technical fields such as the production of semiconductors, in Er doped fibres that function as laser amplifiers, and in high-strength

REE magnets that allow miniaturisation of numerous electronic components used in many appliances (video, computers, etc.). Several REEs are essential constituents of both petroleum fluid cracking catalysts and automotive pollution-control catalytic converters. As a consequence of the increased need, global production of REEs has increased enormously in recent years, paralleled by a fast growing interest in the identification of new ore deposits. Environmental contamination by REEs is expected to grow rapidly in the near future.

Using the data from the FOREGS database, Fedele et al. (2008) investigated anthropogenic sources of REE in Europe with a combination of REE spider diagrams, and interpolated maps showing REE distributions in floodplain and stream sediments, too. These authors concluded that the source of the large-scale distribution patterns of REE over Europe is entirely geogenic. No clear evidence has been found of historic or recent REE contamination from anthropogenic sources, such as the electronics or nuclear industry.

REE distribution maps of Fedele et al. (2008) show that the highest content of REEs in Europe is found in solid media of Italy and the Fennoscandia region. They showed that REE ratios can be used to identify the major plates of the Variscan orogeny and the distinctive granites emplaced after suturing. The Variscan granites caught up in Alpine nappes in Italy were also identified. In Sweden and Italy, similar REEs content occur in solid media related to alkali-rich intrusive rocks (granites and granodiorites) and to alkaline volcanic products of the Latial volcanic area and Campanian Volcanic Zone (Rolandi et al., 2003).

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These volcanic products, mainly of Pleistocene to Holocene age, show REE concentrations comparable to the Swedish REE contents.

However, despite the similarly high REE contents of these bedrocks, the geological context is very different in the two countries. In Sweden, the Ordovician–Devonian age of the alkali granite (emplaced mainly during the Caledonian orogeny) and more recent cryoclastic weathering, favoured the accumulation of REE-rich exploitable rocks. In Italy, the younger age and the Mediterranean climate preserved the alkaline volcanic rocks from erosion, and these outcrops are found today, mainly in densely populated areas. For the time being, there are no plans for the commercial exploitation of REE from volcanic products in Italy, but this possibility cannot be excluded for the future, in response to possible changes in the raw materials market demand.

This work uses the FOREGS REE data for topsoil, subsoil, stream and floodplain sediments, and stream water to identify geogenic and anthropogenic components in young and old bedrock in Italy and Sweden. Notwithstanding the low density of the geochemical survey, it proved useful to provide data necessary to assess the potential mineral resources and anthropogenic influences and data that may be used to determine national-scale REE baselines.

## 2. Data sources

The data used for the present paper were acquired in the framework of the project known as FOREGS (Forum of European Geological Surveys) Geochemical Atlas of Europe, a geochemical baseline project. The main purpose of the project was to generate a harmonised geochemical database for Europe by using the same sampling, sample preparation and analytical methods (Salminen et al., 1998, 2005). The field manual by Salminen et al. (1998) is the basis for a decade-long project, involving geochemists from 26 countries, which led to the publication of the Geochemical Atlas of Europe (De Vos et al., 2006; Salminen et al., 2005). In this framework, Italy and Sweden were divided into eight and eighteen GTN (Global Terrestrial Network) cells ( $160 \text{ km} \times 160 \text{ km}$ ), respectively, following the recommendations of the International Geological Correlation Programme 259 'International Geochemical Mapping' (Darnley et al., 1995). In Italy, at the end of the FOREGS project, the sampling grid has been extended up to a total of 28 cells, including new cells located in coastal areas. The Italian sampling teams, involving three research groups from Napoli, Padova and Siena Universities, collected a total of 50 floodplain sediments, 48 stream waters, 52 stream sediments, 52 topsoils and 47 subsoils. Details of the sampling and analytical methods are given in De Vivo et al. (2008), together with a summary of the main anthropic activities, which might have had an influence on the control of some geochemical anomalies for different elements. In Sweden, a geochemist from the Geological Survey of Sweden, collected 47 floodplain sediments, 51 stream waters, 51 stream sediments, 51 topsoils and 51 subsoils. Methods for planning, sampling, analysis, results and further information are given in the Geochemical Atlas of Europe (De Vos et al., 2006; Salminen et al., 2005).

## 3. Rare earth elements

The REE series (lanthanides) is comprised of 15 elements ranging from 57 to 71 atomic number. They display similar chemical structures, low electronegativity (<1.2) and mostly exist in the trivalent state. Analogies in the physical and chemical properties are due mainly to the REE having the same configuration of valence electrons. The 4f orbitals are gradually filled as the atomic number increases, causing contraction of the ionic radius (also known as the lanthanide contraction), which decreases from 1.16 Å in La to 0.97 Å in Lu. The REEs are divided into two subgroups: LREE (light REE), from La to Eu, and HREE (heavy REE), from Gd to Lu. The overall high oxidation number and large ionic radius of the REE make it difficult for them to enter the lattices of common rock-forming minerals, so they generally are incompatible;

however, the heaviest REE (HREE) have ionic radii small enough to make possible the limited substitution for  $\text{Al}^{3+}$ . REE concentrations in igneous rocks are usually plotted in increasing atomic number order, normalised to chondritic abundance to eliminate the marked change in the concentration of REE of odd and even atomic number. A pronounced peak in REE pattern for Eu, known as the Eu anomaly, is observed due to its bivalent behaviour at low  $f_{\text{O}_2}$ , when it substitutes for  $\text{Ca}^{2+}$  in plagioclase (Eyring, 2006). The Eu anomaly can be positive or negative, in response to the removal or accumulation of plagioclase from magma. Owing to their geochemical features, being relatively stable and insensitive to weathering and hydrothermal alteration, they can be used to determine the primary magmatic history of rocks (Rollinson, 1993). REEs in sedimentary rocks are generally normalised to Post Archaean Australian Shales (PAAS) (Taylor and McLennan, 1985), and REE distribution patterns can be used to understand their sedimentary history. For example, the common  $3^+$  state can be altered to  $2^+$  for Eu, Sm and Yb under strongly reducing conditions, while  $\text{Ce}^{3+}$  can be oxidised to  $\text{Ce}^{4+}$ , hence, highly oxygenated waters, such as seawater, tend to be depleted in Ce on REE plots.

Although there are meaningful variations on the total REE content of igneous rocks with the same degree of evolution, on the whole the total REE content decreases from felsic to mafic terms, being the lowest in komatites (Henderson, 1984). The total REE content in sedimentary rocks is lower than in igneous rocks. As a general rule, elevated REE values are generally indicative of felsic rocks, especially intrusives, and of the sediments derived from them. Finally, since REE are almost insoluble and immobile, their concentrations generally do not vary much during the metamorphic process, and their patterns are overall related to the history of the rock prior to metamorphism.

REEs were originally produced in minor amounts from small deposits in granitic pegmatite, the kind of rock in which they were first found. During the first half of last century, REEs were mainly extracted from placer deposits, particularly those of the southeastern United States, Australia and Russia. Since 1998, more than 80% of the world's REE raw materials have come from China, and most of this production is from the Bayan Obo deposit in Inner Mongolia (Castor and Hedrick, 2006).

## 4. Geological features of the Italian Peninsula and Sweden

### 4.1. Geological features of Italy

Italy underwent many complex orogenic and tectonic phases during its geological history. Main phases are shown on the map of the tectonostratigraphic units (Fig. 1). The lithological map shown in Fig. 2 identifies the correlation between the geological setting and the solid sample media investigated in the present work. All the locations discussed in the text can be found either in Fig. 1 or 2.

The term 'basement complexes' (BCs) is used by Boriani et al. (2003) for the set of rock complexes underlying the post-Variscan unconformity. They show the effects of older deformational, depositional, erosional, metamorphic and magmatic events modified to a variable extent by younger deformational and thermal overprints. To the north, along the Alps, BCs occur as the deepest lithostratigraphic unit in each of the main structural complexes (or nappe systems) making-up the Alpine chain. On the peninsular and insular part of Italy, BCs are exposed in Tuscany (surroundings of Florence) and, more outcrops to the south, in Calabria and Sicily (Calabria–Peloritani Terrane). Finally, BCs dominate on the island of Sardinia, where they are classified into Axial Zone, Nappe Zone and External Zone. The Calabria–Peloritani Terrane is a tectonic juxtaposition of a N subterrane (the Sila and the Serre Massifs) and a S subterrane (Aspromonte Massif and Peloritani Mts.) (Boriani et al., 2003). Most rock types indicate a shallow crustal nature, but intermediate to deep crustal rocks occur both in the Alps (the so called Ivrea–Verbano Zone) and in Calabria. The shallow crustal sequences consist of metapelitic–psammitic rocks of various metamorphic



**Fig. 1.** Map of the main tectonostratigraphic units of Italy.  
modified from Compagnoni et al., 2004.

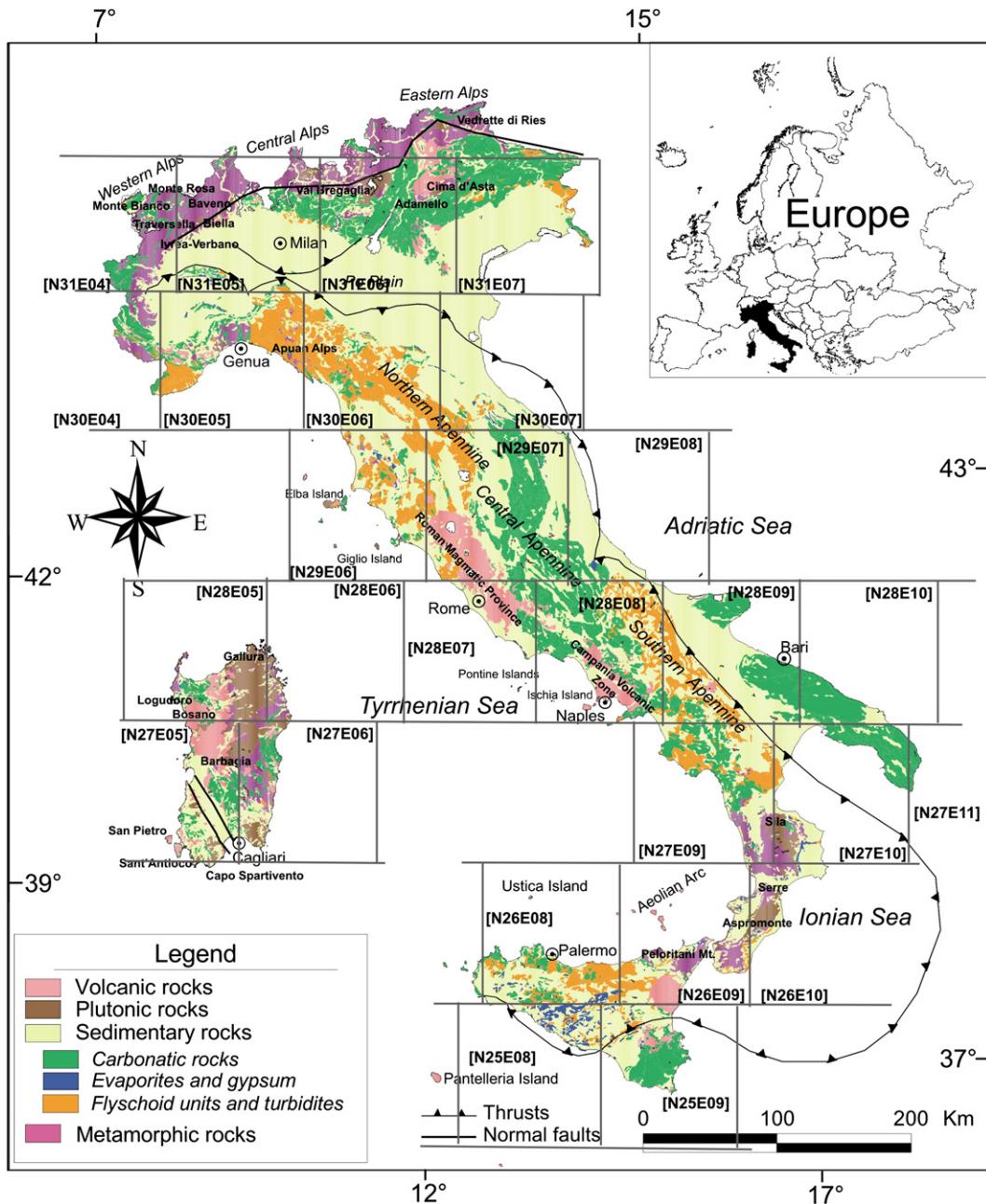


Fig. 2. Lithological map of Italy (modified from De Vivo et al., 2008) with the FOREGS sampling grid.

grade with lenses or intercalations of leucocratic gneiss, amphibolite, felsic and mafic metavolcanics and some marbles. All the BCs rocks, apart from those outcropping in southern Sardinia, were strongly affected by the Variscan metamorphism.

Between the Late Cambrian and the Early Devonian, the Caledonian orogeny occurred as a consequence of the collision, in Western Europe, of Baltica, Laurentia and Avalonia subcontinents. The fingerprints of this orogenic phase are doubtful in Italy, namely in Sardinia, because they are strongly masked by the Hercynian orogeny, known as Variscan in Europe. This phase took place between the Devonian and Early Permian, and led to the formation of a single supercontinent, the Pangaea. Variscan orogeny rocks can be found in the Alps, Sardinia, Calabria, north-eastern Sicily (Peloritani Mountains) and in scattered outcrops in western Tuscany (Apuan Alps). Crustal thickening and polyphase metamorphism characterise the Variscan terrains in Italy. Typical lithotypes are phyllite, gneiss and amphibolite. The presence of a late orogenetic

magmatic phase that occurred between Late Carboniferous and Early Permian is confirmed by the granites and plutonites in western Alps (Monte Bianco and Monte Rosa, Monte Baveno), Cima D'Asta in the Dolomites, Barbagia and Gallura granites in Sardinia, and widespread ignimbrite flows in Trentino Alto Adige. Most of these granites were derived from high-K calc-alkaline magmatism, and have been formed at a regime of lithospheric extension and attenuation affecting the whole domain of the European Hercynian belt (Rottura et al., 1998). On the whole, they display chondrite-normalised REE patterns characterised by variable LREE enrichment and moderate to pronounced negative Eu-anomalies, with no significant HREE fractionation (Rottura et al., 1997).

The end of Variscan orogeny was marked by the extensional reactivation of faults systems that produced new sedimentary basins. During the Late Triassic-Early Jurassic, a major transgression formed an open marine shelf covering most of present central Europe. Submarine

volcanic products were emplaced as pillow lavas, the oldest (Early Jurassic) can be found at scarce outcrops in the southern Apennines and in Sicily, the youngest (Upper Jurassic–Lower Cretaceous) make-up the ophiolitic complexes in the inner Alpine and Apenninic zones. The spreading movement forming Tethys was in the early Triassic, and sedimentation continued until the lower Caenozoic era. During the Alpine orogeny enormous stress was exerted on sediments of the Alpine Tethys basin, and its Mesozoic and early Caenozoic strata were pushed against the stable Eurasian landmass by the northward-moving African landmass. Most of this occurred during the Oligocene and Miocene epochs. The pressure formed great recumbent folds, or nappes, that rose out of what had become the Alpine Tethys and pushed northward, often breaking and sliding one over the other to form gigantic thrust faults. In this framework, the Apennine chain represent a part of the Alpine orogen, experiencing a different evolution from the Alpine chain as a consequence of the complex geodynamic phases, firstly related to the opening of the Sardinia–Corsica basin (ca. 20 Ma) and then of the Tyrrhenian basin, which caused the anticlockwise rotation of the Italian Peninsula. As a consequence of the Alpine orogeny collisional phases, granitic and tonalitic intrusive rocks (Biella, Traversella, val Bregaglia, Adamello and Vedrette di Ries) were emplaced ca. 30 Ma ago.

During the Oligocene, in response to the opening of the Ligurian-Provençal back-arc basin (Speranza et al., 2003), related to the subduction of African oceanic lithosphere under the European continental margin toward the NNW (Beccaluva et al., 1994 and references

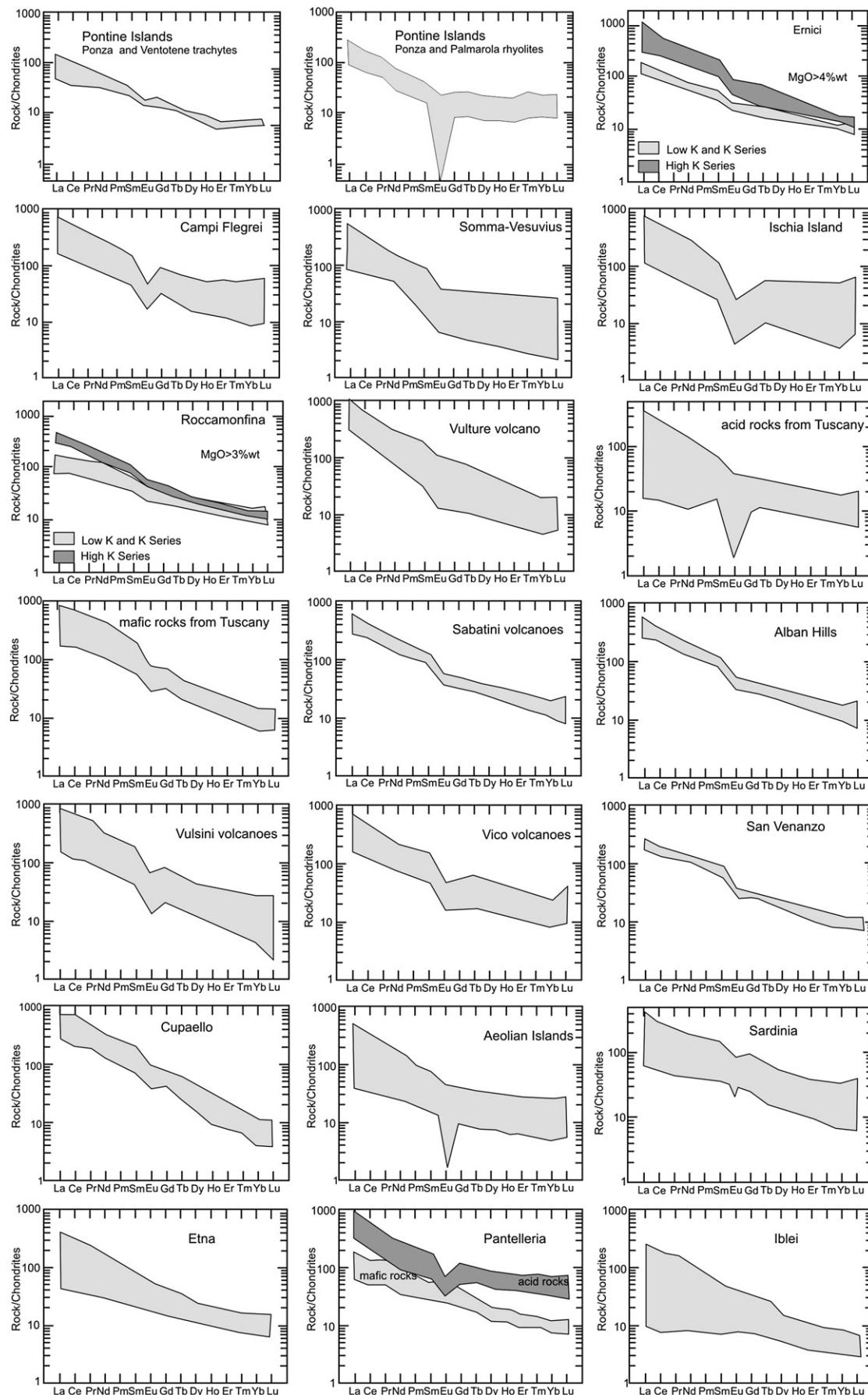
therein), orogenic volcanism took place on Sardinia, with widespread lava flows and felsic ignimbrites in the Cagliari area, the Logudoro-Bosano area, and on San Pietro and Sant'Antioco islands.

Starting from Pliocene, both insular and peninsular Italy became the site of intense volcanic activity. Plio-Quaternary magmatism in Italy exhibits an extremely variable composition, and petrological and geochemical data are used to group the activity in various magmatic provinces, mainly linked to different types of magma genesis (Peccerillo, 2005 and references therein). The Tuscany province (14–0.2 Ma) displays anatetic silicic magmas and minor mantle derived calcalkaline to ultrapotassic mafic rocks. The Roman, Umbria, Ernici–Roccamonfina and Neapolitan provinces (0.8 Ma to present) are formed by mantle derived potassic to ultrapotassic rocks having variable trace element and isotopic compositions. The Aeolian arc (1 Ma to present) mainly consists of calcalkaline to shoshonitic rocks. The Sicily province contains young to active centres (notably Etna) with a tholeiitic to Na-alkaline affinity. Finally, volcanoes of variable composition occur on Sardinia and, as seamounts, on the Tyrrhenian Sea floor. Magmas in the Aeolian arc, and along the Italian Peninsula, have a subduction related geochemical character, whereas the Sicily and Sardinia provinces display intraplate signatures.

For the purposes of the present paper, we partially modified the classification scheme of Peccerillo (2005), and for Pliocene to Present in Table 1, we report the volcanic areas, the age and type of volcanism. As far as REE content is concerned, we used chondrite-normalised plots (Fig. 3) to compare the range of REE contents and patterns of volcanic

**Table 1**  
Volcanic areas, age and type of volcanism from Pliocene to Present in Italy (modified from Peccerillo, 2005).

Magmatic province (ages are in Ma)	Main volcanic centre (age is in Ma, except where otherwise stated)	Type of volcanic centre	Rock type
Tuscany (14–0.2)	Elba (8–6), Montecristo (7), Giglio (5)	Intrusions, aplites, and pegmatites	Granitoids
	Amiata (0.3–0.2), Cimini (1.4–1.1), Tolfa (3.8–1.8)	Domes and stratovolcanoes	Trachydacite to latite lava flows and domes
	Sisco (14), Radicofani (1.3)	Monogenetic extrusive and subvolcanic bodies	Potassic to ultrapotassic (lamproitic) compositions
	Capraia (7.3–3.5)	Stratovolcanoes displaying effusive and explosive activity	High-K calc-alkaline andesite and dacite
Umbria (0.6–0.3)	San Venanzo (0.3), Cupaello (0.6–0.5)	Monogenetic centres and lava flows	Ultrapotassic melilitic (kamafugitic) compositions
Roman province (0.6–0.02)	Vulsini (0.6–0.15), Vico (0.4–0.1), Sabatini (0.6–0.04) Alban Hills (0.6–0.02)	Polyphase volcanoes displaying effusive activity and variable size explosive eruptions	Potassic (trachybasalt, latite, and trachyte) and ultrapotassic (leucite–tephrite, leucite, and phonolite)
Pontine Islands	Ponza (4–1)	Submarine lava domes and hyaloclastites and subaerial lava flows and pyroclastites	Calcalkaline and rhyolite followed by peralkaline, rhyolite and potassic trachyte
	Palmarola (2–1.8)	Submarine lava domes and hyaloclastites	Calcalkaline and rhyolite
	Ventotene (0.8–0.1)	Stratovolcano formed by lava flows and pyroclastic deposits	Basalt, K-trachybasalt to trachyte
Campania volcanic zone (>0.6 to Present)	Roccamonfina (0.6–0.1)	Polyphase stratovolcano displaying effusive activity and variable size explosive eruptions	Mafic to felsic subalkaline to alkaline potassic (KS) and ultrapotassic (HKS) composition
	Somma-Vesuvius (0.04–1944 AD)	Polyphase stratovolcano displaying effusive activity and variable size explosive eruptions	Slightly to strongly silica undersaturated trachybasalt and leucite–tephrite to trachyte and phonolite
	Ernici (0.7–0.1)	Volcanic fields with variously sized monogenetic explosive eruptions and minor effusive activity	Subalkaline (LKB) to alkaline potassic (KS) and ultrapotassic (HKS) mafic composition
	Campi Flegrei (0.08–1538 AD)	Volcanic fields with variously sized monogenetic explosive eruptions and minor effusive activity	Trachybasaltic to trachyphonolitic compositions
	Ischia (0.15–1302 AD)	Volcanic fields with effusive activity and variously sized explosive eruptions	Trachybasaltic to prevailing trachytic compositions.
Vulture (0.7–0.13)	Vulture (0.7–0.13)	Polyphase stratovolcano displaying effusive activity and variable size explosive eruptions	Na–K-rich tephrite, phonolite, and foidite with hauyne
Aeolian Arc (>1 to Present)	Panarea (0.15–0.05), Vulcano (0.12–1888 AD), Lipari (0.2–580 AD), Salina (0.5–0.13), Stromboli (0.2 to Present) Filicudi (1–0.4), Alicudi (0.06–0.03)	Stratovolcanoes displaying effusive and explosive activity	Dominant calcalkaline (basalt, andesite, and rhyolite) and shoshonite compositions
Sicily (7.5 to Present)	Etna (0.5 to Present), Iblei (7.5–1.5)	Stratovolcanoes displaying effusive and explosive activity	Tholeiitic basalt to Na-alkaline composition
Sardinia (5.3–0.1)	Ustica (0.7–0.1), Pantelleria (0.3–0.005), Linosa (1–0.5)		
	Montiferro (4–2) Orosei–Dorgali (4–2)	Stratovolcanoes, flood basalts and monogenetic centres	Tholeiitic basalt to Na-alkaline composition



**Fig. 3.** Chondrite normalised REE plots for Plio-Pleistocene volcanic products of Italy.  
data from Peccerillo, 2005.

products of single areas. The plots show that the Plio-Pleistocene volcanic rocks from Italy are LREE enriched and have negative Eu anomalies which are more evident in the evolved members. On the whole, the highest REE content is shown by Roman (Vulsini and Vico) volcanic centres, Campania (Campi Flegrei, Somma Vesuvio and Ischia) volcanoes and at Pantelleria Island in the Sicily channel. A strong LREE enrichment is found in correspondence to the Vulture volcano, at Campi Flegrei and on Ischia Island. A slight negative anomaly is recorded for Yb at Campi Flegrei, Ischia Island and at Vico volcano.

#### 4.2. Geological features of Sweden

The Fennoscandian Shield comprises an Archaean nucleus in its north-eastern part to which Proterozoic terrains have been successively accreted along the southern and western flanks (Gaál and Gorbatschev, 1987). Sweden is a part of the Fennoscandian Shield and composed of Archaean to Neoproterozoic rocks, and geographically, it can be divided into seven geological regions, each with a distinct tectonic history and geochemical character (Fig. 4). The oldest Archaean rocks are found in northern Sweden in the Kiruna area and between Luleå and Piteå, near Boden (Kathol et al., 2011), and towards Jokkmokk. Most of the Archaean units were generated during the Saamian orogeny (3.1–2.9 Ga), amalgamated by collision at ca. 2.0–1.9 Ga, then reworked during Proterozoic tectonic events to form collisional belts, such as the Lapland granulite belt (Hölttä et al., 2008). The Archaean rocks, in general, consist of mafic and granitoid rocks.

The post-Archaean development started with periods of rifting of the craton interior and its margin between 2.44 and 1.96 Ga (Gaál and Gorbatschev, 1987; Nironen, 1997). The majority of Sweden consists of rocks of the Svecokarelian Orogen, formed during the Palaeoproterozoic in two distinct phases, one between 2.44 and 1.96 Ga and the second between 1.96 and 1.75 Ga. After the accretion was completed, subsequent east- and northward subduction resulted in pervasive reworking of the newly formed crust during the late

Svecfennian (ca. 1.85–1.75 Ga). This reworking resulted in the voluminous Trans-Scandinavian Igneous Belt (TIB) along the south-west margin, as well as penecontemporaneous, mainly granitoid magmatism and regional metamorphism further towards the continent, e.g., in Bergslagen (Andersson, 1991; Andersson et al., 2004; Patchett et al., 1987). The Trans-Scandinavian Igneous Belt (TIB) is situated to the west of the Svecokarelian domain and stretches from southernmost Sweden northwards, beneath the Caledonian mountain chain and up to the coastal region in northern Norway (Högdahl et al., 2004; Sadeghi et al., 2013), and consists of largely undeformed granitoids and associated porphyries. The Bleckinge–Bornholm province is located in southern Sweden. Early amphibolites, felsic metavolcanics, mica schists, and gneisses (ca. 1.77–1.69 Ga) were intruded by tonalite–granodiorite plutons and were not affected by the Sveconorwegian orogeny. The Sveconorwegian orogen predominantly consists of bedrock originally formed during the Gothian orogeny (1.7–1.55 Ga), cut by late Mesoproterozoic igneous rocks (ca. 1.1–0.9 Ga), and subsequently deformed and metamorphosed under amphibolite to granulite–eclogite facies conditions into gneisses, granulites, eclogites, and migmatites. Rare supracrustal rocks (greywacke, quartzite, and shale) occurring with minor mafic to felsic volcanics in south-western Sweden have been metamorphosed under greenschist to amphibolites facies conditions. Neoproterozoic rocks in Scandinavia are represented by sedimentary successions of marine and fluvial sandstones, conglomerates, and carbonates occurring within the Caledonides. In Sweden, the current exposures are mainly composed of Neoproterozoic to Palaeozoic (mostly Silurian) marine to fluvial sediments and volcanoclastic successions, which were deposited at the continental margin of the Iapetus Ocean between ca. 700 and 400 Ma (Gee et al., 2008). Outside the Caledonides, the majority of Phanerozoic rocks are remnants of the Cambro-Silurian sedimentary cover (550–400 Ma old sandstones, shales, and limestones) that once covered much of central and northern Europe. These are found in southern and central Sweden and on the islands of Gotland and Öland. Cambrian to Permian diabase

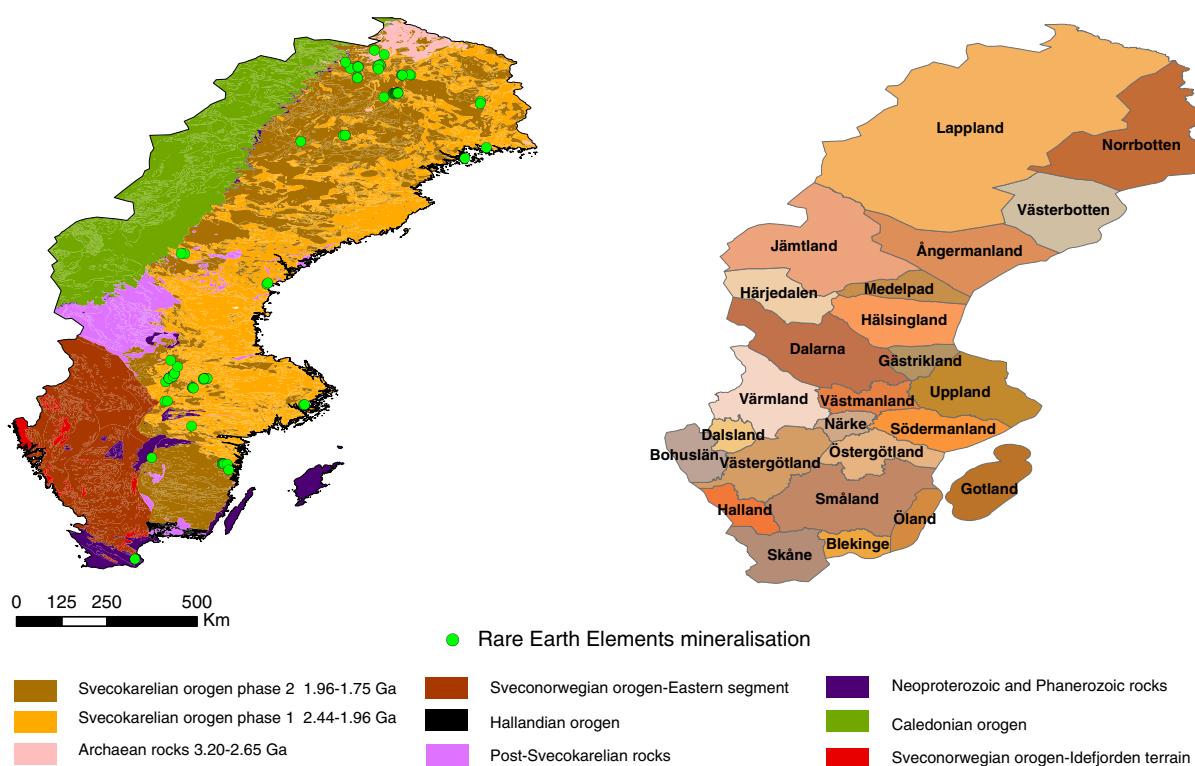


Fig. 4. Geological sketch map (a) and landscape map (b) of Sweden.

**Table 2**

Basic statistical parameters for REE FOREGS data in topsoil, subsoil, floodplain sediment, stream sediment and stream water for Italy and Sweden.

Italy							Sweden						
Element	N	Mean	Median	Minimum	Maximum	Std.Dev.	Element	N	Mean	Median	Minimum	Maximum	Std.Dev.
<i>Topsoil</i>													
La	51	39.628	31.900	6.850	143.000	24.567	La	51	17.421	16.900	6.920	34.300	6.690
Ce	51	78.176	64.000	14.000	267.000	46.100	Ce	51	37.667	35.000	14.000	83.000	15.704
Pr	51	8.763	7.280	1.340	29.200	4.992	Pr	51	4.101	3.910	1.640	8.160	1.631
Nd	51	31.888	27.400	5.410	97.400	16.410	Nd	51	15.135	14.500	6.710	31.800	6.116
Sm	51	5.899	5.180	0.970	15.500	2.693	Sm	51	2.982	2.760	1.370	6.010	1.147
Eu	51	1.196	1.110	0.210	3.170	0.568	Eu	51	0.647	0.630	0.240	1.290	0.231
Gd	51	5.584	5.160	0.860	13.300	2.375	Gd	51	3.074	2.890	1.150	6.400	1.116
Tb	51	0.835	0.770	0.150	1.710	0.314	Tb	51	0.493	0.470	0.220	1.080	0.176
Dy	51	4.490	4.350	0.910	8.860	1.570	Dy	51	2.953	2.940	1.480	6.180	0.944
Ho	51	0.859	0.820	0.170	1.740	0.296	Ho	51	0.613	0.600	0.280	1.340	0.202
Er	51	2.457	2.460	0.550	4.910	0.839	Er	51	1.876	1.800	0.950	3.960	0.576
Tm	51	0.356	0.350	0.100	0.690	0.118	Tm	51	0.284	0.280	0.130	0.570	0.084
Yb	51	2.347	2.370	0.670	4.140	0.766	Yb	51	2.010	1.980	1.080	4.190	0.585
Lu	51	0.342	0.340	0.120	0.620	0.113	Lu	51	0.305	0.300	0.170	0.580	0.080
<i>Subsoil</i>													
La	47	40.504	31.300	15.300	142.000	27.049	La	51	25.188	21.400	12.300	47.100	8.608
Ce	47	78.230	62.600	5.520	267.000	50.238	Ce	51	55.906	48.800	22.700	101.000	18.810
Pr	47	8.996	7.080	3.330	28.200	5.558	Pr	51	5.943	5.370	2.930	11.400	2.045
Nd	47	33.217	27.300	11.400	97.800	19.605	Nd	51	21.859	19.200	12.000	41.100	7.366
Sm	47	6.094	5.140	1.900	15.600	3.180	Sm	51	4.302	3.800	2.300	8.330	1.470
Eu	47	1.244	0.990	0.320	3.160	0.704	Eu	51	0.841	0.780	0.360	1.580	0.278
Gd	47	5.775	5.140	1.820	12.400	2.683	Gd	51	4.248	3.820	2.250	7.890	1.463
Tb	47	0.838	0.740	0.280	1.680	0.347	Tb	51	0.666	0.610	0.360	1.170	0.207
Dy	47	4.460	4.140	1.620	8.250	1.667	Dy	51	3.787	3.550	2.020	7.230	1.190
Ho	47	0.850	0.790	0.320	1.550	0.314	Ho	51	0.777	0.750	0.370	1.470	0.243
Er	47	2.415	2.280	1.010	4.400	0.853	Er	51	2.343	2.240	1.210	4.390	0.695
Tm	47	0.353	0.320	0.130	0.650	0.122	Tm	51	0.362	0.360	0.170	0.650	0.114
Yb	47	2.324	2.190	1.030	4.140	0.783	Yb	51	2.478	2.400	1.280	4.370	0.750
Lu	47	0.337	0.310	0.160	0.620	0.115	Lu	51	0.363	0.350	0.180	0.590	0.104
<i>Stream sediment</i>													
La	51	32.573	27.000	1.400	96.900	18.772	La	51	43.047	37.600	15.800	125.000	22.822
Ce	51	64.598	56.000	2.200	202.000	37.148	Ce	51	94.798	77.400	36.600	301.000	54.305
Pr	51	7.155	6.000	0.300	22.000	4.118	Pr	51	11.385	9.760	4.380	36.100	6.529
Nd	51	28.296	25.200	1.100	84.910	16.328	Nd	51	44.676	37.900	17.300	139.000	25.294
Sm	51	5.453	4.900	0.200	14.300	2.872	Sm	51	8.528	7.250	3.490	24.600	4.753
Eu	51	1.048	0.920	0.050	2.830	0.589	Eu	51	1.373	1.250	0.570	3.390	0.578
Gd	51	4.772	4.610	0.200	9.400	2.214	Gd	51	8.750	7.310	4.050	26.800	4.693
Tb	51	0.712	0.700	0.020	1.320	0.311	Tb	51	1.275	1.030	0.650	4.260	0.680
Dy	51	3.958	3.930	0.110	7.410	1.653	Dy	51	7.055	5.780	3.780	25.300	3.678
Ho	51	0.765	0.800	0.040	1.510	0.306	Ho	51	1.466	1.200	0.740	5.490	0.787
Er	51	2.154	2.200	0.070	4.270	0.894	Er	51	4.365	3.470	2.140	17.300	2.438
Tm	51	0.314	0.320	0.020	0.630	0.124	Tm	51	0.653	0.530	0.350	2.680	0.373
Yb	51	2.014	2.080	0.100	4.080	0.829	Yb	51	4.557	3.760	2.260	18.700	2.547
Lu	51	0.305	0.310	0.010	0.590	0.123	Lu	51	0.708	0.570	0.340	3.010	0.417
<i>Stream water</i>													
La	48	0.060	0.011	0.001	1.050	0.167	La	51	0.991	0.710	0.007	5.320	1.211
Ce	48	0.097	0.017	0.002	1.750	0.289	Ce	51	1.671	1.210	0.006	10.100	2.097
Pr	48	0.013	0.003	0.001	0.200	0.033	Pr	51	0.265	0.190	0.002	1.490	0.329
Nd	48	0.052	0.010	0.001	0.750	0.126	Nd	51	1.022	0.720	0.009	5.760	1.263
Sm	48	0.010	0.002	0.001	0.130	0.023	Sm	51	0.191	0.130	0.001	1.070	0.232
Eu	48	0.004	0.002	0.001	0.021	0.004	Eu	51	0.026	0.016	0.001	0.130	0.029
Gd	48	0.016	0.004	0.001	0.160	0.031	Gd	51	0.184	0.130	0.003	0.970	0.214
Tb	48	0.002	0.001	0.001	0.020	0.003	Tb	51	0.025	0.017	0.001	0.130	0.029
Dy	48	0.009	0.003	0.001	0.110	0.019	Dy	51	0.146	0.099	0.004	0.710	0.164
Ho	48	0.003	0.001	0.001	0.024	0.004	Ho	51	0.031	0.023	0.001	0.140	0.035
Er	48	0.008	0.002	0.001	0.100	0.018	Er	51	0.095	0.066	0.003	0.400	0.105
Tm	48	0.002	0.001	0.001	0.023	0.004	Tm	51	0.014	0.010	0.001	0.060	0.015
Yb	48	0.010	0.002	0.001	0.230	0.035	Yb	51	0.095	0.064	0.004	0.410	0.102
Lu	48	0.003	0.001	0.001	0.052	0.008	Lu	51	0.016	0.011	0.001	0.070	0.017
<i>Floodplain sediment</i>													
La	50	51.684	46.375	14.160	134.000	22.328	La	47	67.685	58.690	34.000	192.000	33.013
Ce	50	25.590	22.850	8.000	71.400	11.821	Ce	47	35.213	29.600	17.000	130.000	19.552
Pr	50	5.778	5.100	1.600	15.000	2.595	Pr	47	7.577	6.600	3.800	27.900	4.268
Nd	50	23.060	20.335	6.300	62.810	10.444	Nd	47	30.432	27.200	15.600	117.000	17.414
Sm	50	4.473	4.250	1.170	10.600	1.791	Sm	47	5.836	5.120	3.210	23.600	3.317
Eu	50	0.945	0.895	0.330	2.170	0.367	Eu	47	1.083	0.970	0.550	3.880	0.546
Gd	50	4.235	4.060	1.100	9.500	1.559	Gd	47	5.424	4.800	2.810	22.610	3.115
Tb	50	0.643	0.605	0.170	1.300	0.230	Tb	47	0.779	0.720	0.400	3.260	0.439
Dy	50	3.737	3.545	1.150	6.750	1.257	Dy	47	4.768	4.330	2.470	19.610	2.612

(continued on next page)

**Table 2** (continued)

Italy							Sweden						
Element	N	Mean	Median	Minimum	Maximum	Std.Dev.	Element	N	Mean	Median	Minimum	Maximum	Std.Dev.
<i>Floodplain sediment</i>													
Ho	50	0.715	0.700	0.220	1.330	0.239	Ho	47	1.022	0.940	0.510	4.470	0.601
Er	50	2.013	1.895	0.700	3.620	0.676	Er	47	2.899	2.620	1.390	12.200	1.698
Tm	50	0.281	0.275	0.110	0.530	0.093	Tm	47	0.439	0.410	0.200	1.890	0.264
Yb	50	1.871	1.805	0.700	3.290	0.644	Yb	47	2.790	2.530	1.230	12.990	1.822
Lu	50	0.280	0.250	0.100	0.520	0.107	Lu	47	0.430	0.390	0.180	2.210	0.310

dykes, porphyritic monzonite, and ultramafic intrusions outcrop in central (Västergötland), western (Bohuslan), and southern (Skåne) Sweden. Triassic through Cretaceous shallow marine sandstones, siltstones, shales, and limestones occur only in the south of the country. All geological regions in Sweden have a variable but generally rather thin soil layer dominated by glacial debris from the last glaciation and marine or post-glacial deposits. Ice transport distances are, however, short and rarely exceed 5–10 km in northern and central Sweden. In the southern part of the country, displacement is more variable and can reach up to 60–80 km (Sohlenius et al., 2009).

## 5. Comparison of REE distribution in Italy and Sweden

**Table 2** reports a summary of basic statistical parameters for the single REEs in each investigated sample medium. For solid media results are reported in mg/kg, and for stream waters in µg/l. In **Table 3**, a description on the REE distribution in the various sample media is reported for Italy and Sweden, together with a brief explanation of the main anomalies. For more details concerning REE distribution and occurrences in Sweden the reader is referred to Sadeghi et al. (2013). Figs. 5a, b, 6a, b and 7a, b show the geochemical distribution maps of Ce, La and Yb in topsoil, subsoil, water, stream sediment and floodplain for both countries. All other REE interpolated maps are available as electronic supplementary material. These maps were prepared by using ArcView® software, using the inverse distance weighted (IDW) algorithm to generate a regular grid. The advantage of IDW method is that the information contained in a punctual sample will be preserved during the interpolation. (Lima et al., 2003; Sadeghi et al., 2013).

### 5.1. Residual soil

The lowest values of total REE t in topsoil are 40.47 and 54.32 mg/kg, the highest 119.33 and 619.99 mg/kg for Italy and Sweden, respectively. The lowest values of total REE in subsoil are 120.53 and 72.88 mg/kg, and the highest 714.79 and 297.88 mg/kg for Italy and Sweden, respectively.

Both LREE and HREE are enriched in the Italian soil samples of the Latial–Campanian alkaline volcanism area. Enrichment is most evident for LREE (e.g., La and Ce). Anomalous REE enrichment is generally also found in soil samples from the eastern Sardinia, the Euganei Hills and Iblei Mountains. These values seem to reflect the presence of alkali igneous products in the bedrock. High REE contents are recorded also in soil samples where the arenaceous bedrock is mostly made-up of volcanic clasts (e.g., the Arenarie Val di Sabbia substratum, consists of andesitic clasts, corresponds to a topsoil and subsoil with high Dy content). As far as Swedish soil samples are concerned, the highest REE contents are generally correlated with the presence of evolved granites. For all REE, median and maximum contents are higher in Italy than in Sweden.

Boxplots for Ce, La and Yb in topsoil and subsoil (**Fig. 8**) show that, mainly for LREE, Italian soil samples display overall higher contents with respect to their Swedish counterparts, and that the range of values for Italy is larger than what is recorded for Sweden. The main difference

in topsoil and subsoil data for the two countries is that the highest values in Italy are recorded in topsoil, whereas in Sweden in subsoil.

### 5.2. Stream sediment

The lowest values of total REE content in stream sediment are 7.32 and 121.72 mg/kg, and the highest 487.32 and 786.36 mg/kg for Italy and Sweden, respectively.

In Italy for most REE high and very high concentrations are recorded in Latium, in the Neapolitan volcanic area, along the Calabria–Peloritani arc including eastern Sicily and in eastern Sardinia, where catchment basins are mainly made-up of Quaternary volcanic rocks or of metamorphosed crystalline basement. Stream sediment samples tend to reflect the REE contents of the rocks outcropping in the areas crossed by the tributary rivers and streams, but they also correlate quite well with REE contents in residual soil samples.

In Sweden, the distribution of REE content in stream sediment samples is quite similar to that of residual soil and, besides the presence of alkali granite in the catchment basins, it often reflects mineralisation (e.g., Sm enriched stream sediment due to pegmatitic REE mineralisation in the northern part of Sweden) or secondary concentrations related to clay-rich stream sediment, mainly in the southern part of Sweden. Furthermore, a strong correlation of REEs with U and Th in granite–pegmatite rocks and felsic volcanics in the northern part of Sweden is recorded (Sadeghi et al., 2013). Boxplots comparing REE contents in stream sediments in Italy and Sweden (electronic Supplementary material) show the opposite situation with respect to soil. Swedish stream sediment samples, in fact, are much richer in all the REE in comparison to the Italian ones, and the variation range of data for the former is much larger.

### 5.3. Floodplain sediment

The lowest values of total REE content in floodplain sediment samples are 42.6 and 94.54 mg/kg, and the highest 346.6 and 205.49 mg/kg for Italy and Sweden, respectively.

REE contents in Italian floodplain sediment reflects the REE contents of the bedrocks outcropping in the areas, and maximum values are generally recorded in areas where alkaline volcanic and igneous products outcrop (Latium and Campania along the Tyrrhenian coast, Etna and Iblei Mts.). High to moderate contents mainly of HREEs are recorded in floodplain sediment samples along the eastern Alpine boundary and in Liguria, where they likely reflect the presence of a chaotic complex of clays with heterogeneous inclusions of ophiolites, that are LREE depleted (Rampone and Borghini, 2008). However, the possibility that clay-rich sediments could be REE-enriched owing to secondary phenomena cannot be excluded.

Floodplain sediment samples in Sweden are generally REE-enriched in mineralised areas (e.g., Ho enrichment of Västerbotten and Lapland, related to sulphide and iron apatite mineralisation, respectively), or where river beds have high concentrations of Al, K and are clay-rich, as in the south-eastern part of Sweden in Uppland, Södermanland, Belkinge, and Skåne. Boxplots (electronic SUPPLEMENTARY material) show that floodplain sediment samples in Sweden are more REE-rich than their Italian counterparts.

**Table 3**  
REE distribution and occurrences in the five investigated media for Italy and Sweden.

REE	Country	Soil	Stream sediment	Foodplain sediment	Stream water
Ce Fig. 5a, b	Italy	The highest Ce values ( $>125$ mg/kg in topsoil and $>130$ mg/kg in subsoil) are recorded in the Roman and Neapolitan volcanic provinces, and in the northern Piemonte area. The strongest anomaly occurs in Campania region around the Roccamonfina extinct volcano (267 mg/kg both in topsoil and subsoil). These anomalies can be related to the high LREE content of the volcanic bedrock.	The highest contents of Ce ( $>130$ mg/kg) occur in northern and southern Latium. High values (around 100 mg/kg) are also recorded in scattered areas of northern Italy, in Apulia, Calabria, and eastern Sicily, mostly related to the volcanic or metamorphic rocks outcropping in these areas.	The lowest Ce values occur in south-western Sardinia and in southern Italy; the highest, on the counterpart, in the volcanic area of northern Latium. Moderately high Ce values are recorded in the Alpine region along the Swiss-Italian border and in the Napoli area.	Very low Ce values characterise the whole of northern Italy, south-west Sardinia and are scattered across Sicily. High Ce concentrations ( $>1 \mu\text{g/l}$ ) occur in the volcanic areas of Roman-Campania province, where the highest value is found around the Roccamonfina volcano.
Dy	Sweden	Topsoil and subsoil Ce distribution map in Sweden show similar anomalies, where the highest values (80 mg/kg and 101 mg/kg in topsoil and subsoil, respectively), recorded in central (Jämtland), south-east (Småland), and south-west Sweden (Bohuslän), correlate with evolved granites. The Ce anomalies in northern Sweden can be related to Fe mineralisation e.g. Kiruna-type of apatite-iron deposits (Sadeghi et al., 2013).	The highest Ce anomaly in Sweden is related to Svecokarelian organic rocks in the southern part of Sweden in the Småland, Öland area. In addition, some anomalies are related to evolved granite in the northern part within the Caledonian terrain.	The lowest Ce anomaly reflects the Sveconorwegian bedrock units in the western part of Sweden. Cerium enrichment occurs where river beds have high Al and K concentrations, and are clay-rich, as in the south-eastern part of Sweden in Uppland, Södermanland, Belkinge, and Skåne. High Ce occurs in the most part of the Caledonian orogen and in the Västerbotten area, where it is related to mineralisation.	Very low Dy values characterise northern Italy and Sicily. High Dy concentrations ( $>0.012 \mu\text{g/l}$ ) occur in the volcanic areas of Roman-Campania province, and around Vulture volcano in Basilicata, reflecting the mixing with waters circulating in REE enriched volcanic products.
Er	Italy	Highest Dy concentrations in topsoil occur in the Latium-Campagna volcanic area, with the highest values in northern Latium. High values are also recorded in northern Tuscany. The subsoil pattern is very similar, with the highest values recorded along the Tyrrhenian coast where volcanic products outcrop; on the whole, these high values reflect the presence of mainly felsic volcanic products in the bedrock. Two more sites, located in north-central and north-eastern Italy, display high Dy values in subsoil (7.03 and 8.21 mg/kg, respectively); the former on arenaceous bedrock, Arenarie Val di Sabbia, the main components of which are andesitic volcanic clasts (Cassinis et al., 2008), and the latter on Carnian basin deposits.	Dysprosium concentrations are much higher in northern than in southern Sweden. High values are located mainly in soil overlaying the crystalline basement and loess/palaeoplaicer area of northern Sweden (Lapland), and also in the northern part of the Caledonian terrain and Jämtland area.	Highest Dy values occur in the northern and southern parts of Sweden, in the Öland related to the Svecokarelian orogen phase 2. Mostly, they show a good correlation with Th and U.	High Dy concentrations occur in the southern part of Sweden related to the Sveconorwegian evolved granites. The highest Dy anomaly occurs in Västerbotten where the main mineralisation is related to felsic volcanic rocks. Caledonian terrain rocks also show slightly higher Dy anomaly compared to the other parts of Sweden.
					Very low Er values are associated with felsic rocks in north-western Alps and in the Roman volcanic area.
					Very low Er values characterise southern Sardinia, Sicily and most of the Italian Peninsula. A high anomalous concentration is found in Campania region, north of Napoli, possibly reflecting the mixing with water circulating in shallow water tables in volcanic terrains.

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**Table 3** (continued)

REE	Country	Soil	Stream sediment	Foodplain sediment	Stream water
Eu	Sweden	High Er values are found mainly on the crystalline basement with granitic composition and in palaeoplacer areas in northern Sweden (Salpeter et al., 2005).	The highest Er concentration occurs in the northern part of Sweden and is related to the crystalline granitic basement (Sadeghi et al., 2013).	The highest Er anomalies occur in Västerbotten and eastern part of Kiruna area in the northern part of Sweden, and are associated with mineralisation. The second high Er concentration occurs in Caledonian terrain.	High Er concentrations occur in the southern part of Sweden, and are associated with granites and felsic Proterozoic rocks.
Gd	Italy	Europium in topsoil and subsoil shows very similar distribution patterns with the highest values ( $>1.7 \text{ mg/kg}$ in topsoil and $>2 \text{ mg/kg}$ in subsoil) recorded in the Roman and Neapolitan volcanic areas, whereas the lowest contents are found in north-western Alps and southern Tuscany. On the whole, they reflect the Eu enrichment trend of bedrock, as it is the case of the anomalous enrichment in the Veneto region, related to the Euganei Hill alkali-basaltic bedrock.	The Eu anomalies are similar to the topsoil and subsoil in the northern part of Sweden, but anomalies also occur in the southern part of Sweden in Öland and Småland related to the younger evolved granitoids.	The lowest Eu anomaly occurs over the Sveconorwegian bedrock units in the western part of Sweden, similarly to the other REE. Most part of the Caledonian orogen shows high concentrations of Eu compared to other parts of Sweden. The high values of Eu also occur in the Västerbotten area in the northern part of Sweden, where they reflect mineralisation occurrences. A moderate range anomaly occurs in the south-eastern part of Sweden in Uppland, Södermanland, Blekinge and Skåne.	High Eu concentrations in the southern part of eastern Alps. High Eu concentrations ( $>0.005 \text{ µg/l}$ ) occur along the Tyrrhenian coastline, in the Mount Vulture area, in Central Calabria and south-western Sardinia, reflecting the mixing with waters circulating in contact with alkaline bedrock.
Ho	Italy	Highest Gd concentrations in topsoil are found in the Latium–Campania volcanic area and in the northern Apennine. A similar behaviour is displayed by Gd in subsoil, with the highest concentrations in Latium and Campania; anomalous high values are also found in Veneto and western Lombardy (distribution similar to the Eu), reflecting the enrichment trend of the bedrock. The areas with high Gd concentrations in Sweden overlap with Eu anomalies (Sadeghi et al., 2013).	High Gd concentrations are recorded in the volcanic areas of Latium and Campania, eastern Sardinia, north-eastern Sicily and central Calabria. Gd in Öland, in southern part of Sweden, possibly related to anthropic activity.	The highest Gd values are recorded in northern Latium and southern Tuscany, but values are quite high for the whole of northern Italy, eastern Apulia and eastern Sicily (basaltic rocks outcropping at Punta delle Pietre Nere and at Etna and Iblei). Lowest values occur in western Sardinia and at few scattered sites of southern Apennine, most of which on limestone basement.	Very low Gd values characterise southern Sardinia, Sicily and the most part of Italian Peninsula. Two anomalous high values are found in Campania, north of Napoli, and along the Ionian coast of Apulia, possibly related to anthropic activity.
				The lowest Gd anomaly occurs in south-western Sweden similarly to the other REE. Caledonian orogen shows high concentration of Gd; also there is a high value of Gd in the Västerbotten related to mineralisation. Moderate anomalies occur in the south-eastern part of Sweden in Uppland, Södermanland, Blekinge and Skåne related to higher content of clay minerals.	High Gd concentrations in the southern part of Sweden are associated with granites and felsic Proterozoic rocks.

Sweden	High Ho values in northern Swedish soils are found in areas with crystalline basement rocks. High Ho concentrations in Swedish soils are strongly correlated with high Gd, Tb, and Dy concentrations.	Ho anomalies occur in northern and southern parts of Sweden, where they are related to granitic–pegmatitic lithologies enriched in U and Th (Sadeghi et al., 2013).	The lowest Ho anomaly occurs in south-western part of Sweden, similarly to the other REE distribution. The highest Ho concentrations occur in two parts of Västerbotten and Lapland, where they are related to sulphide and iron apatite mineralisation, respectively. Caledonian bedrock shows also moderate to high Ho concentration. The lowest La values occur over most of Calabria, in south-western Sardinia and over the whole of north-eastern Italy. An anomalous high values area is located north of the Roman alkaline province	High Ho concentrations in the southern part of Sweden are associated with granites and felsic Proterozoic rocks. Very low La values characterise northern Italy and Sicily. High La concentrations ( $> 0.023 \mu\text{g/l}$ ) occur in the alkalic volcanic areas of Roman–Campania provinces, and at Vulture volcano in Basilicata.
La Fig. 6a,b	Italy	High and very high La values are found in Latiun and Campania regions where volcanic alkaline rocks outcrop and at a few scattered sites of northern Italy, mainly where the bedrock is represented by alkaline plutonic rocks.	The low La contents ( $< 25 \text{ mg/kg}$ ) occur in a narrow area of the central Alps and in north-eastern Italy. Moderately high La values are found along the Tyrrhenian coast, northern Sicily, central Apulia, eastern Sardinia and north-eastern Italy, with an anomalous high value in an area between Veneto and Trentino, where it reflects the occurrence of alkali basaltic rocks; the highest La values ( $> 50 \text{ mg/kg}$ ) are recorded in northern Latium–southern Tuscany and in the Neapolitan volcanic area.	La anomalies show a pattern similar to Ce. The weakest La anomaly occurs in Sveconorwegian bedrock units in the south-western part of Sweden. The highest Ce value occurs in the Västerbotten area in the northern part of Sweden where it is related to mineralisation. La is enriched in the south-eastern part of Sweden in Lapland, Småland, Skåne and Blekinge, where river beds have high Al and K concentrations and are clay-rich. High La values occur over most part of the Caledonian orogen.
Sweden	The main La anomalies in Sweden occur in northern Sweden in Lapland associated with granite and pegmatite, and in central Sweden in Jämtland; some narrow anomalies occur in the southern part of Sweden in Öland, and are related to younger granitic rocks.	La anomalies occur in the southern part of Sweden related to clay-rich stream sediments (secondary La concentrations); migmatised bedrock with well-developed leucosome is another possible source of high La in sedimentary cover in the northern part of Sweden (Sadeghi et al., 2013).	The highest Lu values occur in the Swiss Alpine sector, eastern Liguria and southern Tuscany. Very low concentrations are found across many areas of central and southern Italy, in south-eastern Sicilia and in north-eastern Italy.	Low Lu values characterise the whole of the Italian Peninsula, with only two anomalous values higher than $0.03 \mu\text{g/l}$ in the Neapolitan volcanic area.
Lu	Italy	In topsoil, high Lu values are predominantly found along the coast of Latiun and Campania, where alkalic volcanic products occur, but also in several areas of northern Italy, where mainly flyschoid clay-rich deposits outcrop, and at a single point in northern Apennines (inner Tuscany), where the bedrock is mainly made-up of marly-limestones. Lu distribution in subsoil is very similar to the topsoil, with high and very high values in central and southern Italy, west of the Apennine chain, and in north-easternmost Italy, all soils mainly developed on alkaline igneous bedrock.	The highest Lu contents ( $> 0.4 \text{ mg/kg}$ ) are found associated with volcanic, crystalline and metamorphic rocks in the catchments basins of central Calabria, eastern Sardinia, eastern Sicily, central and northern Latium and southern Trentino. Low Lu concentrations occur in most areas of northern Italy and at few sites of central Apennine.	The weakest Lu anomaly in floodplain sediments occurs in south-western part of Sweden similarly to the other REE distribution. The highest Lu concentration occurs in two parts of Västerbotten and Lapland where it is related to sulphide and Fe-apatite mineralisation, respectively. Caledonian bedrock shows also medium to high Lu concentration.
Sweden	Low Lu concentrations in soil occur in areas with metavolcanic rocks and younger granitoids in central and northern Sweden, reflecting the post-Svecokarelian rocks in the western part of Sweden. High Lu contents occur in the Palaeoproterozoic granite–pegmatite series in northern and south-eastern Sweden (Sadeghi et al., 2013).	The spatial distribution of Lu in stream sediment shows similar trends to soil, even if the anomalous area in the southern part of Sweden is narrower. The highest Lu concentration occurs in the Latiun area, related to palaeoproterozoic rocks. There are strong correlations among Lu, Yb, and Tm.	The highest Lu concentrations are found in south-western Sardinia, over most of southern Italy, including southern Campania, where mainly limestone rocks outcrop. The highest values occur in the volcanic area of northern Latium. Moderate Nd values ( $ca. 30 \text{ mg/kg}$ ) characterise northern Campania, southern Apulia, north-eastern Sicily and some scattered points of northern Italy.	Low Lu concentrations in the southern part of Sweden are associated with granites and felsic Proterozoic rocks.
Nd	Italy	Topsoil and subsoil show very similar distribution patterns where the highest values ( $> 50 \text{ mg/kg}$ in topsoil and in subsoil) are recorded in the Latiun and Campania volcanic areas.	The highest contents ( $> 60 \text{ mg/kg}$ ) occur in southern Latium and north of Napoli, while moderately high values ( $ca. 40 \text{ mg/kg}$ ) are found in eastern Sardinia, north-eastern Sicily and western Veneto, all related to the occurrence of Eocene alkali-basalts, whereas in central Calabria, they are related to metamorphic Variscan basement. The lowest values are found in northern Italy, mainly in Liguria and at a few scattered sites of northern Apennine.	Low Nd values characterise stream water of most of northern and central Italy, Sicily and Sardinia. High Nd values are found in Roman–Neapolitan volcanic areas and at Mount Vulture.

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**Table 3** (continued)

REE	Country	Soil	Stream sediment	Foodplain sediment	Stream water
Nd	Sweden	Positive Nd anomalies correspond to the occurrences of crystalline rocks, particularly Archaean rocks in the northern part of Sweden, while the low values in Dalarna and southern part of Sweden correlate with sedimentary rocks, e.g., Dala sandstone, Cambro-Silurian limestone and shale, and younger Mesozoic sedimentary rocks in Skåne in southern Sweden (Sadeghi et al., 2013). Lower Nd concentrations in topsoil in the southern part of Sweden may be related to the glacial deposits over crystalline bedrock of Palaeoproterozoic rocks.	The highest Nd concentrations occur in the southern part of Sweden in Öland related to granitic rocks and in the northern part of Sweden related to gneiss basement and some in Lapland related to granitic bedrock units. The REE mineralisation. The lowest values show a distribution similar to that in soil.	Nd, La, and Ce show very similar patterns in Swedish floodplain sediments. The lowest Nd anomaly occurs in south-western part of Sweden related to Sveconorwegian bedrock units. The highest Nd value occurs in the Västboten area in the northern part of Sweden where it is related to mineralisation. The Nd anomalies also occur in Lapland, Småland, Skåne and Blekinge, where there is a high Al and K concentration and presence of clay-rich sediments in river beds. High Nd values occur over most part of the Caledonian orogen.	High Nd concentrations in the southern part of Sweden are associated with granites and felsic Proterozoic rocks.
Pr	Italy	In topsoil, high Pr values are predominantly found along the coast of Lazio and Campania, where alkaline volcanic products occur; the distribution of Pr in subsoil is very similar, and sensitive to the presence of alkaline volcanic rocks in the substratum.	The highest Pr contents ( $>12 \text{ mg/kg}$ ) are found between southern Tuscany and northern Latium, and north of Napoli. Moderately high concentrations occur in Central Calabria, eastern Sicily, eastern Sardinia and Apulia. All the latter anomalies generally reflect the occurrence of alkaline volcanic products in the catchment basins. Praseodymium anomalies in Sweden mimic to a large extent the Ce anomalies; they show highest levels in the northern part of the country. Other Pr anomalies in Sweden occur in the southern part of Sweden in Öland, showing mostly the same distribution as other REEs.	The Pr distribution pattern in Swedish floodplain sediments is very similar to other REEs, particularly La, Ce, Nd. The highest anomaly occurs in Västboten, related to granitic bedrock and mineralisation. There is a good correlation between Caledonian terrains and high Pr anomalies; in contrast, the weakest Pr anomaly occurs in the south-western part of Sweden related to Sveconorwegian rocks.	Very low Pr values characterise on the whole the Italian Peninsula, including Sicily and Sardinia. The only few sites showing higher Pr concentrations are located in the Roman–Neapolitan volcanic area and at Mount Vulture.
Sm	Sweden	Praseodymium distribution in both topsoil and subsoil in Sweden is very similar. The highest anomaly in Sweden occurs in Lapland and is related to rocks of granitic composition; in subsoil, it is related to rocks of the Caledonian terrain. A single anomaly in Caledonian terrain, both in topsoil and subsoil, is associated with REE mineralisation in pegmatite at the boundary between Caledonian and Palaeoproterozoic terrains. In both topsoil and subsoil the Sm distribution maps show the highest Sm concentrations along the Latin–Campania Tyrrhenian coast, in the volcanic alkaline province. Throughout the rest of Italy the Sm contents are low to very low for both media, and the lowest values ( $<2 \text{ mg/kg}$ ) are recorded in eastern Liguria–northern Tuscany, in Apulia and in Marche regions.	The pattern of Sm distribution is quite homogeneous in almost all Italy. Moderately high Sm concentrations are recorded in eastern Sardinia, Apulia, central Calabria and north-eastern Sicily, together with two single points between Trentino and Veneto regions, where the river catchment basins are mainly made-up of alkali basalts products. Anomalous high concentrations ( $>10 \text{ mg/kg}$ ) are recorded in southern Tuscany, northern Latium and north of Napoli.	The highest Sm values are found in the Roman alkaline volcanic products, but moderately high values are also recorded in northern Campania, eastern Liguria, and eastern Veneto and in the Alps along the Italian–Swiss border. Lowest values occur in southern Sardinia and in most part of central-southern Apennines.	Very low Sm contents characterise stream waters in the most part of northern and central Italy and only a few sites, mostly located in the Roman–Neapolitan alkaline province and at Vulture volcano, record higher values ( $>0.05 \mu\text{g/l}$ ).
Sm	Italy	The highest Sm anomaly occurs in the northern part of Sweden and is related to granitic rocks and Fe apatite mineralisation. In the Jämtland area, there is a single anomaly related to the REE mineralisation in the Caledonian terrain (Sadeghi et al., 2013).	Locally, Sm contents are high in stream sediments in northern parts of Sweden. Two single point anomalies are highlighted in the Swedish stream sediments, the first associated with the pegmatitic REE mineralisation in the northern part of the country and the second occurring in Öland area.	The highest Sm concentration occurs in Västboten and Caledonian terrains. The lowest Sm concentration reflects younger Sveconorwegian granitic composition.	Low Sm contents characterise stream waters in the southern part of Sweden are associated with granites and felsic Proterozoic rocks.
Tb	Italy	Terbium distribution patterns in topsoil and subsoil are very similar. High and very high Tb values are found in the area where volcanic alkaline products outcrop and at a few scattered sites of northern Italy, mainly located in the Tuscan and Emilia Apennines. Low concentrations ( $<0.6 \text{ mg/kg}$ for both media) occur in Eastern Liguria, northern Tuscany, along the Adriatic coast of Marche and Apulia and on Sicily.	Low Tb contents ( $<0.5 \text{ mg/kg}$ ) occur in Friuli Venetia Giulia, most of Lombardy, Piemonte and Liguria, and in the eastern sector of central-southern Apennine. High Tb values ( $>1 \text{ mg/kg}$ ) are found in northern Sardinia and in northern Campania; moderate to high values (ranging between 0.8 and $1 \text{ mg/kg}$ ) characterise northern Latium, Apulia, central Calabria and eastern Sicily, reflecting the Tb contents of the rocks of the catchment areas	On the whole, Tb contents in stream waters are quite low, with the only exceptions being northern Latium, northern Campania and Vulture volcano in Basilicata.	

Tb	Sweden	The Tb anomalies display the same distribution as those of Lu. The higher concentrations of Tb are found in regions with igneous rocks, mostly granitic to pegmatitic in composition. In the southern part of Sweden, some anomalies may be related to the glacial deposits overlying crystalline bedrock (Sadeghi et al., 2013). The lowest Tb concentration reflects younger Sveconorwegian granitic composition.	The Tb distribution patterns show a strong similarity with those of Sm, Pr and Tm.	The highest Tb concentration in floodplain sediments occurs in Västbotten and Caledonian terrains.	High Tb concentrations in the southern part of Sweden are associated with granites and felsic Proterozoic rocks.
Tm	Italy	In the Tm distribution map the highest Tm contents ( $>0.45 \text{ mg/kg}$ ) occur in the Latium volcanic area, central-southern Calabria and eastern Sicily volcanic area. The highest anomaly ( $0.63 \text{ mg/kg}$ ) occurs in north-east Sardinia. The lowest values are found in Friuli Venetia Giulia.	Lowest Tm concentrations are found in south Sardinia, over most of southern Italy and north-easternmost Italy. The highest values occur in the volcanic area of northern Latium and eastern Liguria.	Thulium values in stream water are very homogeneous throughout Italy, and the highest concentration is found in the Napoli neighbourhood.	High Tm concentrations in the southern part of Sweden are associated with granites and felsic Proterozoic rocks.
Yb Fig. 7ab	Italy	The median Tm value in Swedish stream sediment is slightly higher than that of Italian stream sediments. A reason for this is the strong correlation of REE with U and Th in granite-pegmatite rocks and felsic volcanics in the northern part of Sweden (Sadeghi et al., 2013).	High Tm values occur in south-western part of Sweden, similar to the other REE, reflecting Sveconorwegian granitic rocks. The highest Tm values occur in the Västerbotten and Lapland areas where they are related to sulphide and Fe apatite mineralisation, respectively. Caledonian bedrock shows also moderate to high Tm concentrations.	Very low Yb values characterise stream waters over the whole of the Italian Peninsula, including Sicily and Sardinia. The only few sites showing meaningful Yb concentration are located in central Italy and at Mount Vulture (Basilicata). The highest point anomaly ( $>0.23 \mu\text{g/l}$ ) occurs in the Roman-Neapolitan alkaline volcanism area.	High Tm concentrations in the southern part of Sweden are associated with granites and felsic Proterozoic rocks.
Sweden	Italy	In topsoil, high Yb values are predominantly found in the eastern Friuli area, and over the alkaline volcanic lithotypes of the Roman–Neapolitan province, in southern Campania and eastern Tuscany, where the highest value ( $4.14 \text{ mg/kg}$ ) is recorded. The distribution of Yb in subsoil displays very similar features, but high contents are found along the west coast of Italy and in central Apennines; the highest value ( $14.4 \text{ mg/kg}$ ), in the eastern territory, is recorded in the easternmost Alps, along the Austrian–Slovenian border. The spatial distribution of Yb is similar to that of Tm and Er, but areas with elevated values of these elements are generally narrower. High Yb values in soil are located mainly in regions underlain by the crystalline basement, mainly granitic in composition and in areas with high-grade metamorphic rocks (amphibolite, migmatite, granulite, and eclogite) with garnet as a common phase (Sadeghi et al., 2013); some anomalies occur in the Bergslagen area (Västmanland) where they are associated with Yb mining area. Palaeoplaformer area in northern Sweden has higher Yb concentrations as well (Salpeteur et al., 2005).	The highest Yb contents ( $>3.0 \text{ mg/kg}$ ) are found in the Roman volcanic area, over crystalline rocks of central Calabria, in the magmatic area of north-eastern Sicily, in the Alps along the border with Austria and at a single sampling point between Veneto and Trentino. The highest and widest anomaly is recorded in the western sector of Sardinia ( $>3.5 \text{ mg/kg}$ ), where the lithology is mainly represented by pre-Permian basement rocks.	The distribution pattern of Yb shows the lowest values in southern Sardinia and most of southern Italy, including Sicily. High Yb values are found over the Swiss alpine sector pertaining to Italy, and at two scattered points in south-western Lombardy and southern Veneto. An anomalous high value is found in Apulia ( $2.31 \text{ mg/kg}$ ), possibly linked to intense agricultural activity. The highest Yb values ( $>2.5 \text{ mg/kg}$ ) occur in a narrow coastal belt from eastern Liguria to the north of the Roman alkaline province.	Very low Yb values characterise stream waters over the whole of the Italian Peninsula, including Sicily and Sardinia. The only few sites showing meaningful Yb concentration are located in central Italy and at Mount Vulture (Basilicata). The highest point anomaly ( $>0.23 \mu\text{g/l}$ ) occurs in the Roman-Neapolitan alkaline volcanism area.
			The concentrations of Yb in Swedish stream sediments are slightly higher than in Italian stream sediments. There are strong correlations of Yb with U and Th in stream sediments, possibly due to substitution of these elements in heavy minerals commonly found in stream sediments (e.g., garnet).	The distribution pattern of Yb shows highest values in Västerbotten and Lapland, related to sulphide and Fe apatite mineralisation, respectively. There is also a positive anomaly over Caledonian terrain which, generally, shows higher REE concentration.	High Yb concentrations in the southern part of Sweden are associated with granites and felsic Proterozoic rocks.

#### 5.4. Stream water

The lowest total REE values in stream water samples are 0.02 and 0.076 µg/l, and the highest 5.26 and 29.31 µg/l for Italy and Sweden, respectively.

Italian stream waters are generally REE poor, with the only exception of stream waters from the Roman–Neapolitan and Mount Vulture volcanic areas. The highest values recorded at Mount Vulture probably are due to mixing of stream waters with spring waters circulating in shallow water tables located in volcanic REE-enriched terrains.

Two anomalous high Gd values are found to the north of Napoli in Campania, and on the Ionian coast of Apulia. They could be linked to the contamination of stream waters with waste waters. Anomalies found in densely populated areas can be the result of usage of organic Gd compounds, such as the derivatives of the gadopentetic acid (Gd-DTPA), used as a contrast medium in magnetic resonance imaging. After excretion from the human body, the Gd complex enters the surface water mostly by the body effluents and is stable at least six months under natural conditions (Knappe et al., 2005).

Stream water samples show very different features between Italy and Sweden. In Italy, REE content is generally very low and shows a narrow variation range, with a few outlier for each element. In Sweden, stream waters are much more REE-rich and the variation range is much larger.

In Italy, the areas where the maximum REE contents in soil, floodplain and stream sediment samples are recorded coincide fairly well to the areas where stream waters are REE enriched. In Sweden, however, the behaviour of stream water with respect to residual soil is completely the opposite, because the highest values of all REE in stream water samples are recorded in southern Sweden, where the lowest values for both topsoil and subsoil occur. There is nevertheless correspondence of high REE contents in stream water that are located in southern Sweden to maximum REE values in floodplain and stream sediment samples. The distribution maps of all REEs in stream water over Sweden are very similar. The main anomalies occur in the southern part of Sweden, where most of the outcrops of the younger felsic rocks of the Fennoscandian shield can be found. High concentrations of REE in the southern part of Sweden generally dominate the dispersion patterns.

The areas of Småland and Hälsingland are characterised by the low pH in the stream water and high concentrations of dissolved organic matter (DOC). Mineralised regions are generally not discernible, though weak anomalies in Lapland (heavy REEs) and along the coast of Västerbotten (Varuträsk, light REEs) may reflect the presence of pegmatite-type mineralisations.

### 6. Principal component analysis

Multivariate statistics can be used to evaluate a large amount of data in order to identify patterns within a data set that would otherwise be overlooked (Davis, 1986). Principal component analysis (PCA) reduces a large data matrix into two smaller matrices called principal component (PC) loadings and PC scores, which are produced using Eigen analysis. One of the main advantages of PCA is that data do not need to be normally distributed (Johnson and Wichern, 2002). Eigenvalues describe the amount of variation within the original data set explained by each PC. The PC loading, and the elements of the eigenvectors, indicate the relative contribution of each element to the PC score (Stetzenbach et al., 1999). A loading of zero would indicate no relationship between the PC and the original variable (element).

We performed PC analysis on different media (topsoil, subsoil, stream sediment, stream water and floodplain sediment) using the data from the FOREGS database for Sweden and Italy. Plots of loadings of REEs on PC 1, 2 and 3 for topsoil data sets in Italy and Sweden are given, as an example, in Fig. 9. The complete results on number and

name of clusters, based on plots of loadings of REEs on PC 1, 2 and 3 are summarised in Table 4, which shows loadings, eigenvalues and cumulative variance for PC 1, 2 and 3 in the two countries. In order to show which sample belongs to which factor, PCs score plots in topsoil, as an example, are available as electronic supplementary material for both Italy and Sweden.

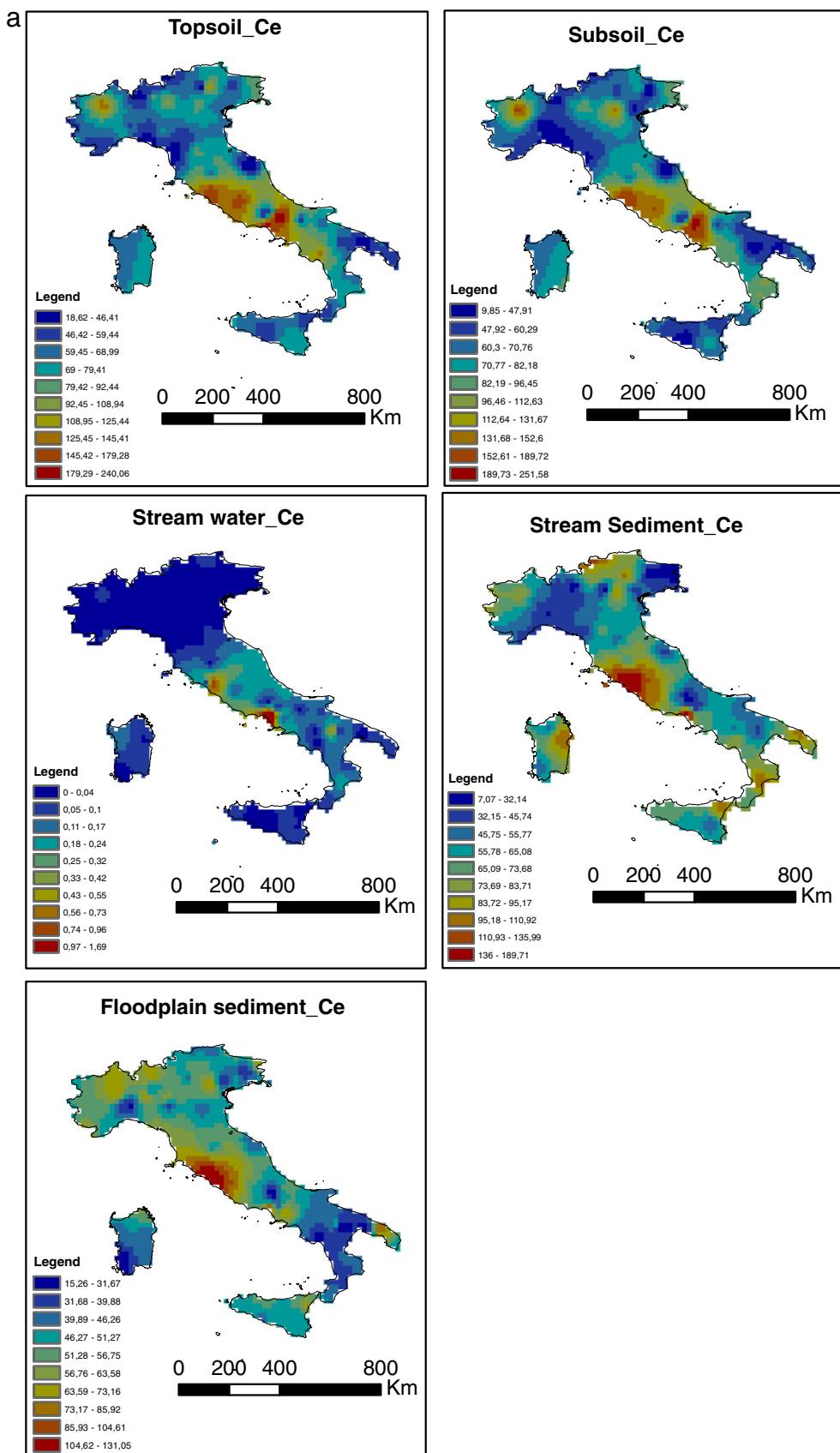
In topsoil, PC1 and PC2 explain 84.8% and 12.1% of total variance, respectively, in the data on Italian samples, and 82.6% and 12.8% of total variance, respectively, in the data on Swedish samples. For subsoil, PC1 and PC2 explain 83.0% and 13.6% of total variance, respectively, on Italian samples, and 83.7% and 12.1% of total variance, respectively, on Swedish samples. For stream sediment, PC1 and PC2 explain 90.2% and 7.67% of total variance, respectively, on Italian samples, and 86.5% and 11.7% of total variance, respectively, on Swedish stream sediment samples. In floodplain sediment, PC1 and PC2 explain 91.6% and 5.51% of total variance, respectively, on Italian samples, and 91.7% and 6.92% of total variance, respectively, on Swedish floodplain sediment samples. Finally, for stream water, PC1 and PC2 explain 74.3% and 19.6% of total variance, respectively, on Italian samples, and 96.7% and 2.06%, respectively, on Swedish stream water samples.

All REE have negative loading on PC1 of data for individual sampling media (Table 4). The LREE have strongest loadings on PC2 for individual sampling media. For topsoil data in Italy, Ce and Lu have the strongest positive loadings on PC3, whereas Eu has the weakest negative loading on this component. For topsoil data in Sweden, Ce has the strongest positive loading on PC3, whereas Eu has the weakest negative loading on this component. For subsoil data in Italy and Sweden, Ce has the strongest positive loading on PC3, whereas Eu has the weakest negative loading on this component. For stream sediment data in Italy, Lu and Ce have the strongest loading on PC3, whereas Eu has the weakest negative loading on this component. For stream sediment data in Sweden, Ce has the strongest loading on PC3, whereas Eu has the weakest negative loading on this component. For floodplain sediment data in Italy, Lu has the strongest positive loading on PC3, whereas Dy has the weakest negative loading on this component. For floodplain sediment data in Sweden, Ce has the strongest positive loading on PC3, whereas Eu has the weakest negative loading on this component. And finally, for stream water data in Italy, Gd has the strongest positive loading on PC3, whereas Eu has the weakest negative loading on this component. For stream water data in Sweden, Ce has the strongest positive loading on PC3, whereas Gd and Pr have the weakest negative loading on this component.

The results on plots of loadings of REE on PC1, PC2 and PC3 (Fig. 9) are summarised in Table 5. Italian and Swedish data sets for individual sampling media show slightly different multivariate structures (Table 5).

In Italian topsoil, the PC1 and PC2 loadings plot shows the contrast between LREE and HREE, which is similar to the Swedish data set. The Italian PC1 and PC3 show two distinct clusters (one comprising most REE and one Eu), which may be related to the occurrence of Eu<sup>2+</sup>, the concentration of which is mainly controlled by the content of organic matter and clay minerals during the stages of weathering. Whereas, the Swedish data set shows three distinct clusters (Eu, Ce and other REEs), which may relate to the origin for each element and any other weathering or mineralisation (Sadeghi et al., 2013). The principal component results for subsoil on Italian and Swedish data sets are similar to those of topsoil, and in Italy the stream sediment results are similar to those of topsoil and subsoil.

Whereas in Sweden, stream sediment plots of PC2 and PC3 loadings of REE show two clusters (Eu and other REE). In the Italian floodplain sediment data set, the plot of PC1 and PC2 loadings shows two clusters, whereas in Swedish samples it shows three distinct clusters (Ce, LREE, and HREE), which may be related to weathering and mineralisation. Plots of PC2 and PC3 loadings for Italian floodplain sediment samples show three clusters (Eu, LREE, and HREE), whereas



**Fig. 5.** Interpolated maps for Ce data in all the investigated sample media for Italy (a) and Sweden (b).

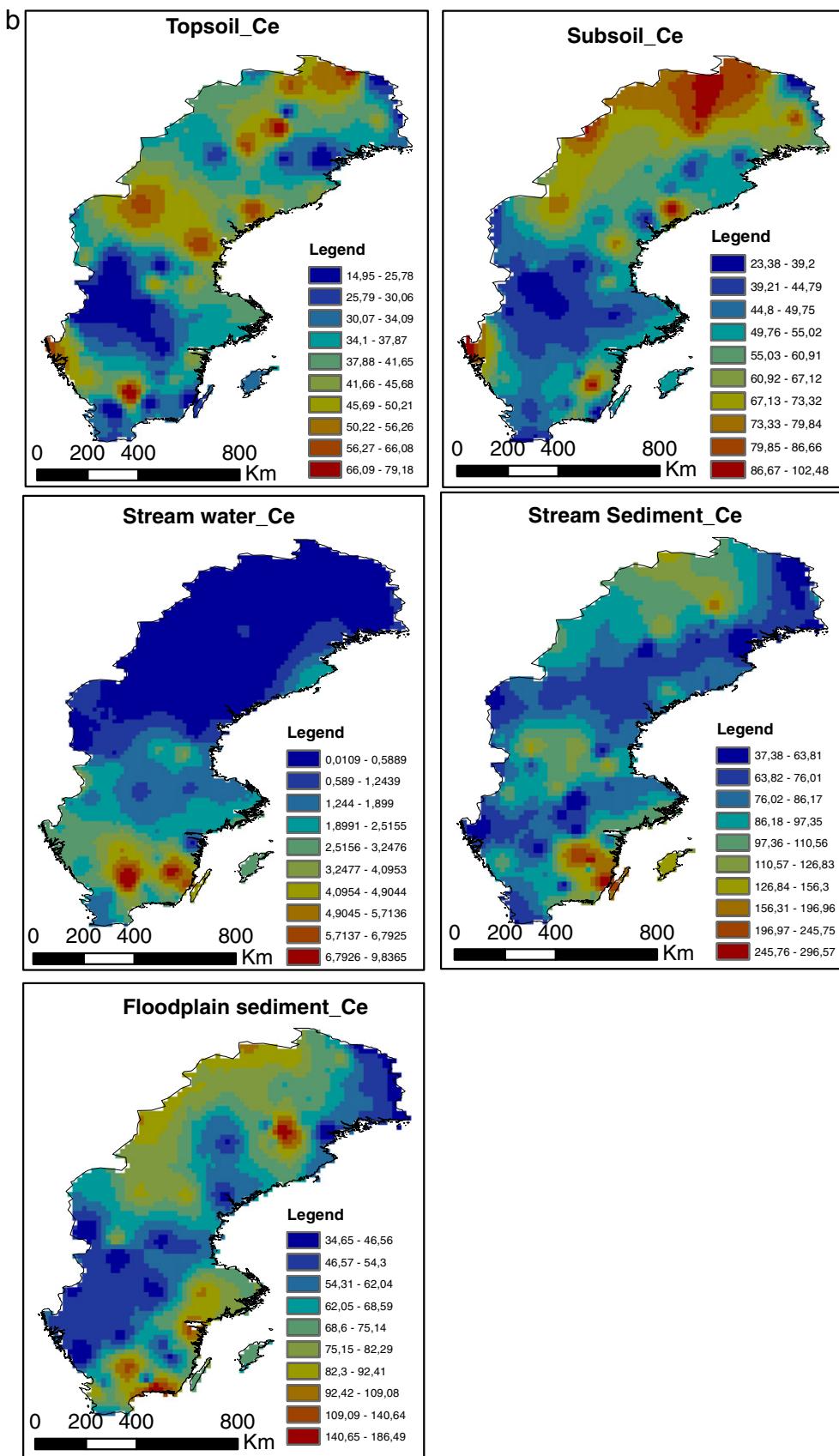
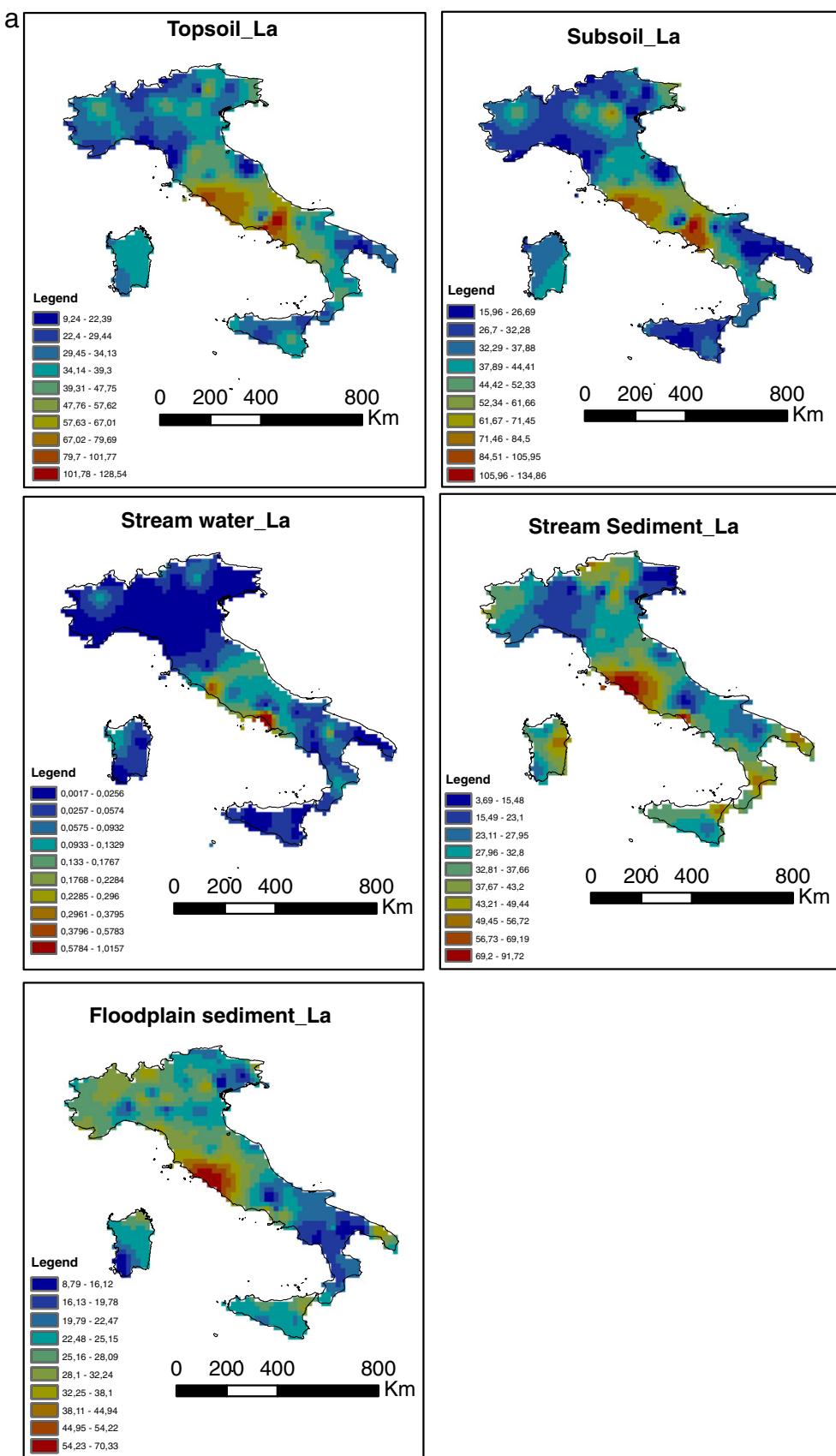


Fig. 5 (continued).



**Fig. 6.** Interpolated maps for La data in all the investigated sample media for Italy (a) and Sweden (b).

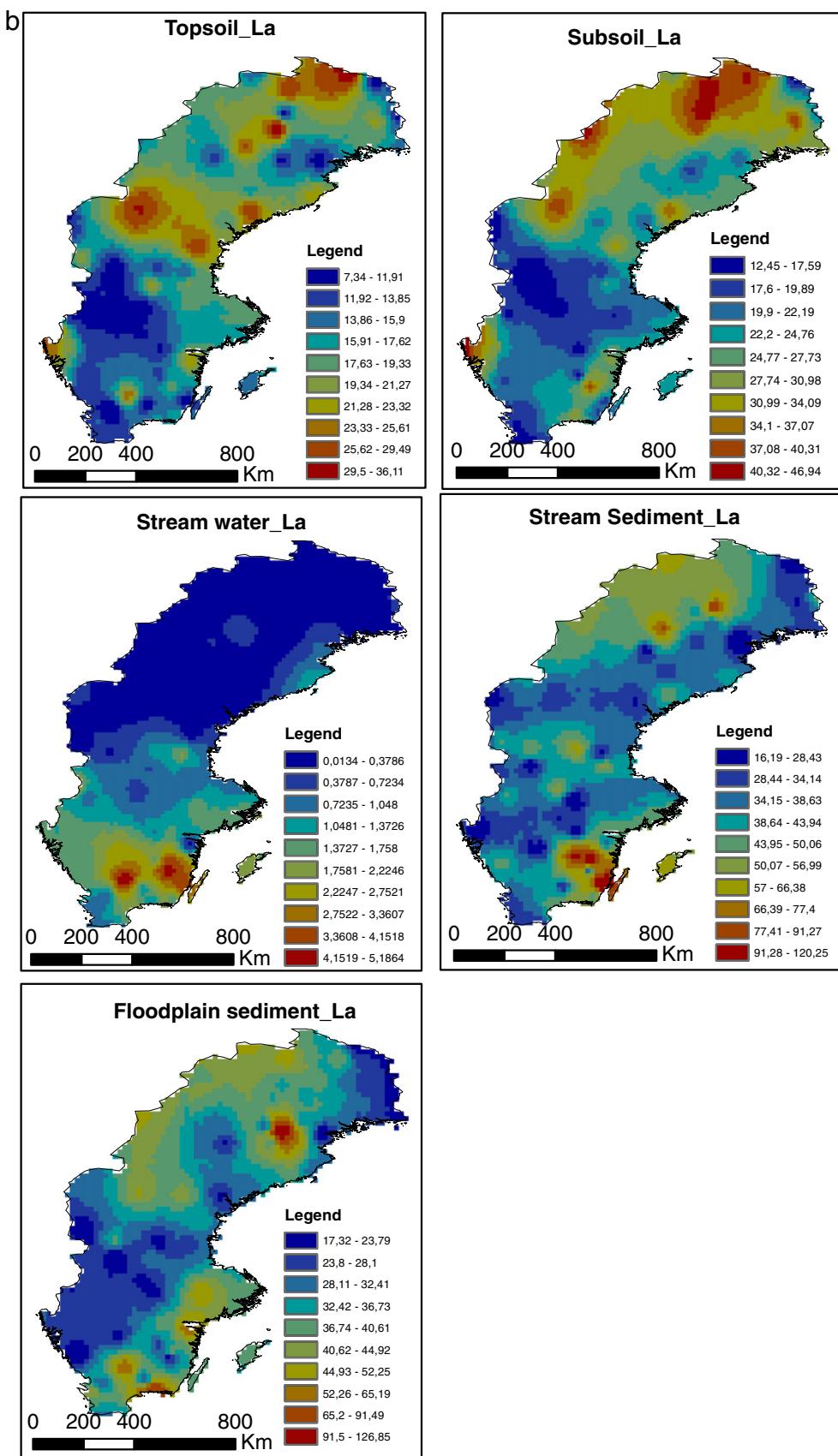
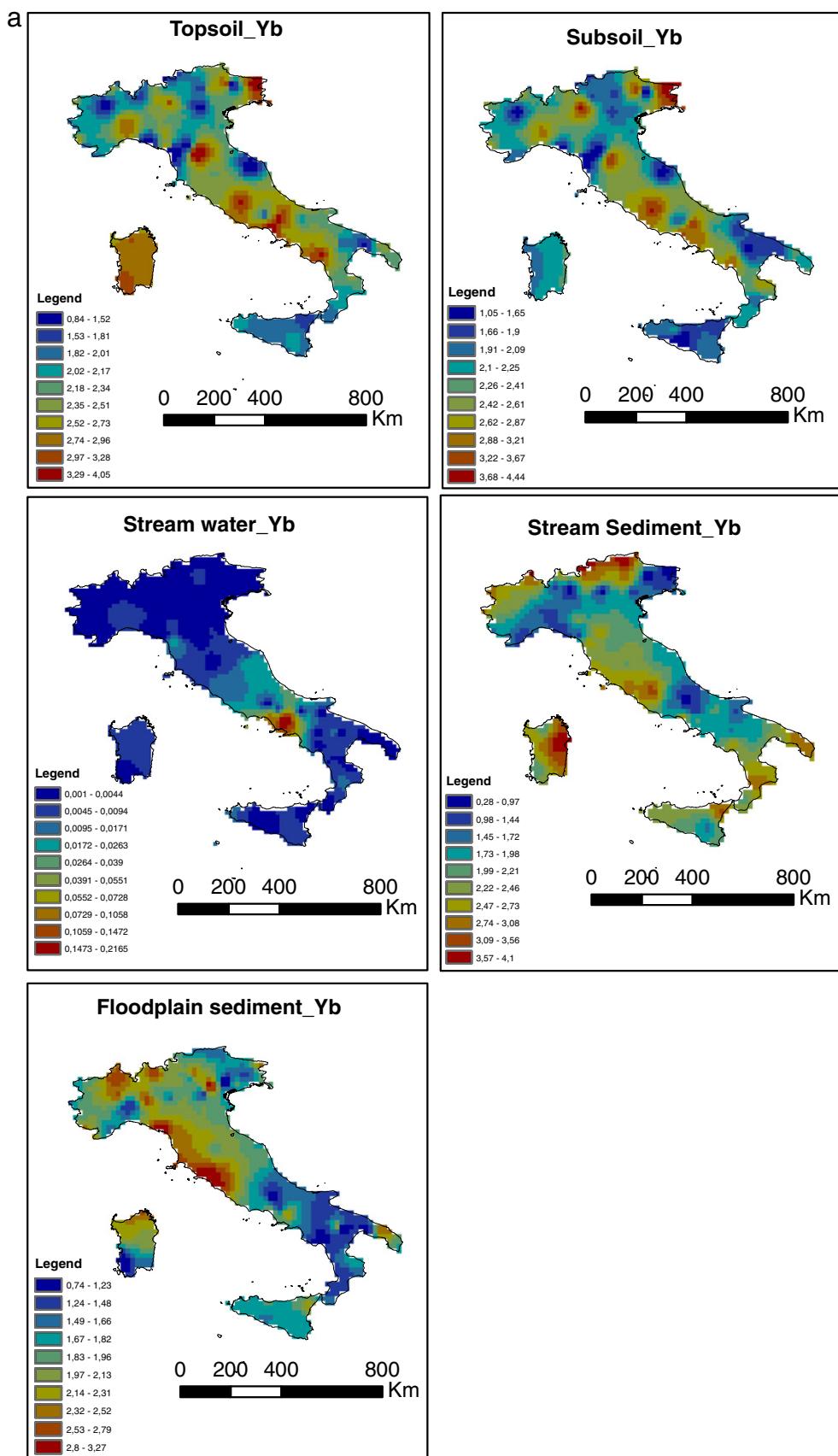


Fig. 6 (continued).



**Fig. 7.** Interpolated maps for Yb data in all the investigated sample media for Italy (a) and Sweden (b).

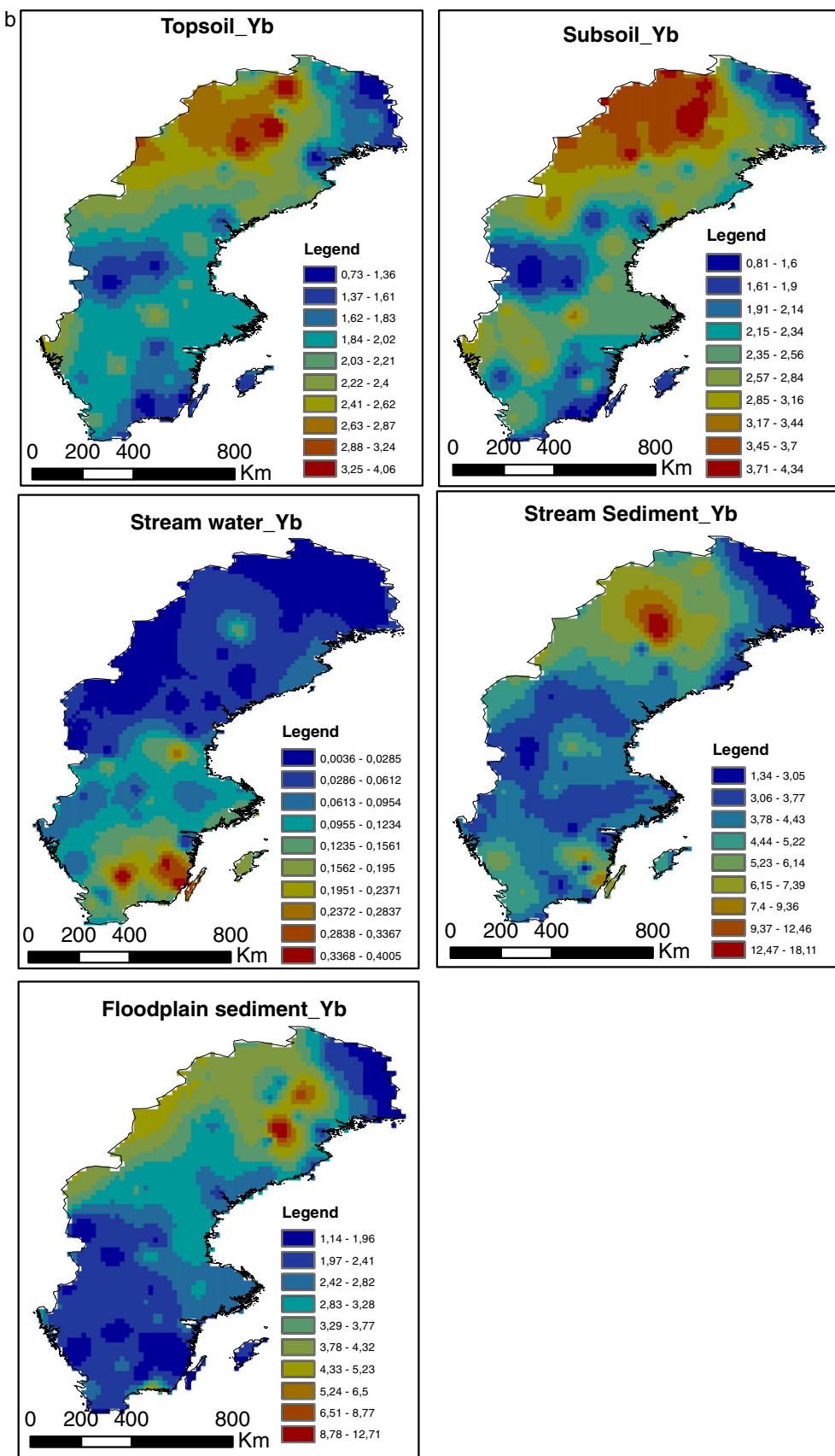
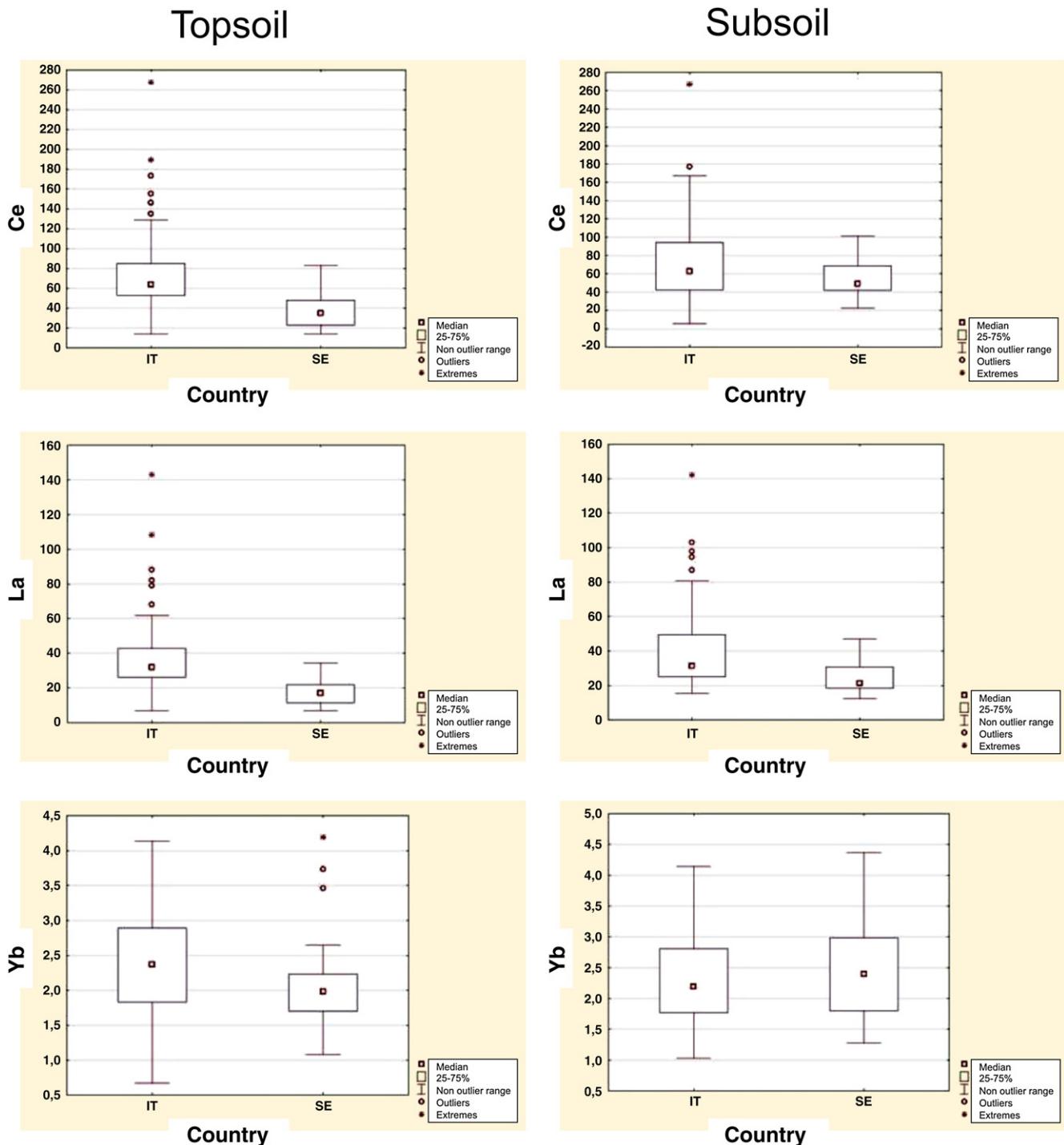


Fig. 7 (continued).



**Fig. 8.** Boxplots for La, Ce and Yb for all the investigated sample media in Italy and Sweden.

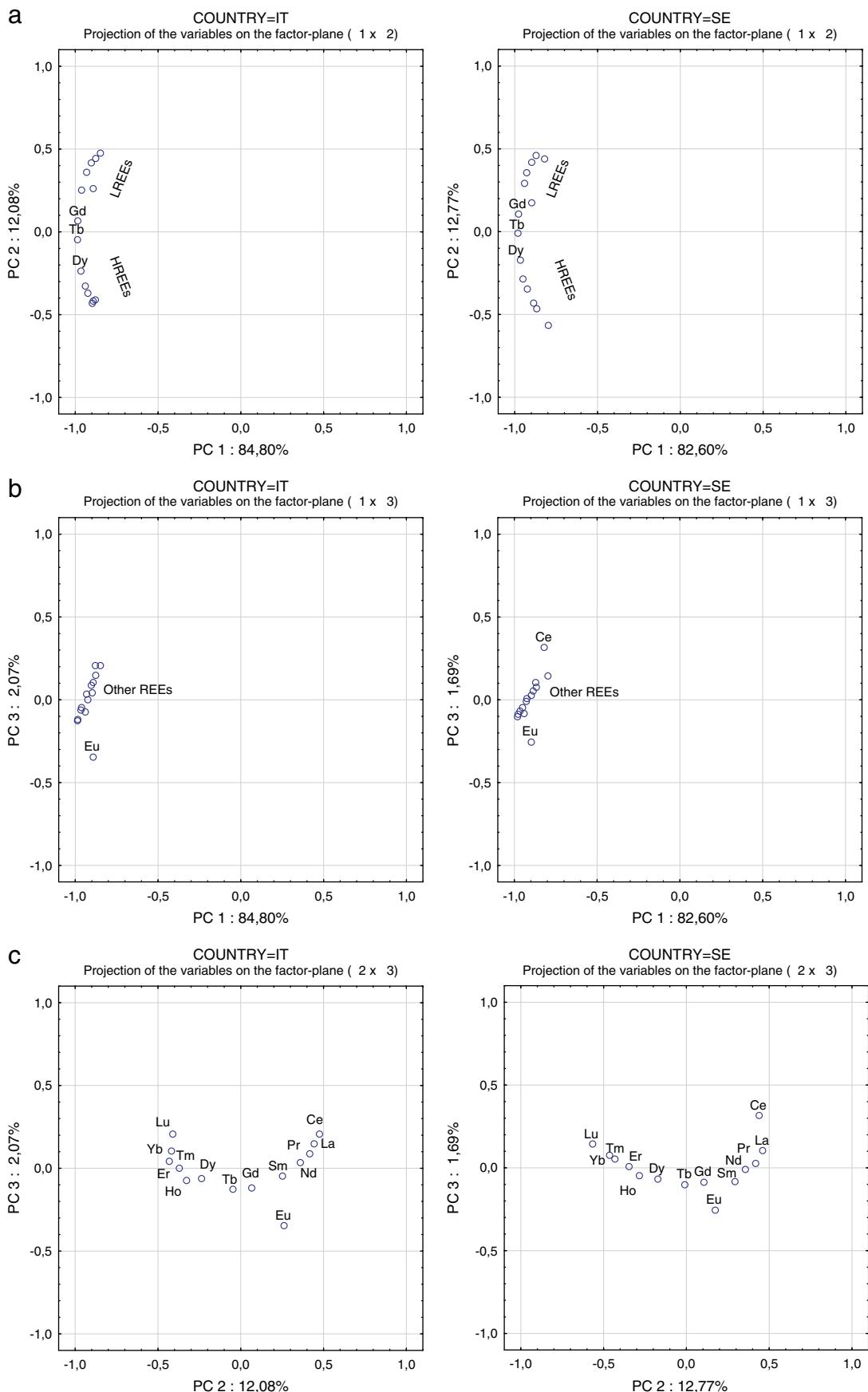
in Swedish samples they show only two clusters (Eu and other REE). Plots of PC1 and PC3 loadings for Italian floodplain sediment samples show two clusters (Lu and other REE) which may relate to anthropogenic sources, whereas in Swedish samples the plot shows three distinct clusters (Eu, Ce and other REE), related to mineralisation and weathering processes controlling each REE.

Italian and Swedish data sets for stream water samples show slightly different multivariate structures. Plot of loadings of REE on PC1 and PC2 in Italian samples shows three different clusters compared to other media (LREE, Eu-Gd, and HREE), whereas in Swedish samples it shows two clusters (LREE and HREE). The results of loading

of REEs on PC1 and PC3 on Italian stream water samples show three clusters (Gd, Eu and other REE), which may relate to pH conditions and anthropogenic sources, whereas Swedish samples show two clusters (Eu and other REE). Finally, the plot of loadings of REE on PC2 and PC3 shows three clusters (Gd, Eu and other REE) in Italian samples, and two clusters (Eu and other REE) in Swedish samples.

## 7. Discussion

Data distribution shows that in both countries the REE contents in soil are sensitive to the geological substratum and that, at least at the



**Fig. 9.** Principal component analysis of Italian and Swedish topsoil data sets. Correlation of elements with PCs: (a) PC1 versus PC2; (b) PC1 versus PC3 and (c) PC2 versus PC3. Notation: IT = Italy; SE = Sweden.

**Table 4**

Correlation between REEs and principal component loadings, Eigenvalues, % variance explained and cumulative % variance for PC1, PC2 and PC3.

Element	Italy			Sweden		
	PC1	PC2	PC3	PC1	PC2	PC3
<i>Topsoil</i>						
La	−0.255	0.341	0.274	−0.256	0.345	0.214
Ce	−0.246	0.365	0.383	−0.241	0.328	0.648
Pr	−0.262	0.320	0.164	−0.264	0.313	0.055
Nd	−0.270	0.276	0.062	−0.273	0.267	−0.018
Sm	−0.279	0.193	−0.089	−0.277	0.219	−0.168
Eu	−0.259	0.201	−0.642	−0.264	0.130	−0.524
Gd	−0.286	0.051	−0.222	−0.287	0.079	−0.177
Tb	−0.286	−0.036	−0.234	−0.289	−0.006	−0.210
Dy	−0.280	−0.182	−0.117	−0.284	−0.129	−0.139
Ho	−0.272	−0.251	−0.136	−0.279	−0.213	−0.097
Er	−0.268	−0.285	−0.001	−0.272	−0.259	0.016
Tm	−0.261	−0.331	0.077	−0.261	−0.322	0.110
Yb	−0.259	−0.321	0.194	−0.255	−0.348	0.158
Lu	−0.255	−0.316	0.384	−0.235	−0.424	0.295
Eigenvalue	11.9	1.69	0.289	11.6	1.79	0.237
% variance explained	84.8	12.1	2.07	82.6	12.8	1.69
Cumulative % variance	84.8	96.9	98.9	82.6	95.4	97.1
<i>Subsoil</i>						
La	−0.880	0.433	0.153	−0.858	0.485	0.081
Ce	−0.784	0.526	0.285	−0.837	0.460	0.228
Pr	−0.909	0.403	0.071	−0.910	0.401	0.039
Nd	−0.926	0.369	0.015	−0.929	0.349	−0.005
Sm	−0.958	0.266	−0.071	−0.967	0.208	−0.026
Eu	−0.901	0.277	−0.312	−0.882	0.250	−0.377
Gd	−0.982	0.104	−0.137	−0.977	0.083	−0.034
Tb	−0.990	−0.007	−0.121	−0.989	−0.022	−0.023
Dy	−0.967	−0.212	−0.104	−0.960	−0.207	0.008
Ho	−0.936	−0.334	−0.057	−0.946	−0.294	0.011
Er	−0.898	−0.428	−0.022	−0.909	−0.383	0.033
Tm	−0.880	−0.439	0.123	−0.902	−0.391	−0.006
Yb	−0.876	−0.450	0.121	−0.882	−0.442	0.059
Lu	−0.844	−0.496	0.149	−0.845	−0.479	0.031
Eigenvalue	11.6	1.90	0.312	11.7	1.70	0.210
% variance explained	83.0	13.6	2.23	83.7	12.1	1.50
Cumulative % variance	83.0	96.5	98.8	83.7	95.8	97.3
<i>Stream sediment</i>						
La	−0.945	0.302	0.105	−0.880	0.458	0.052
Ce	−0.947	0.297	0.116	−0.804	0.571	0.106
Pr	−0.945	0.304	0.110	−0.920	0.387	0.031
Nd	−0.947	0.304	0.085	−0.942	0.331	0.015
Sm	−0.971	0.229	0.022	−0.976	0.195	0.013
Eu	−0.899	0.330	−0.248	−0.907	0.207	−0.367
Gd	−0.986	0.023	−0.081	−0.992	0.062	0.041
Tb	−0.984	−0.058	−0.137	−0.994	−0.062	0.021
Dy	−0.977	−0.139	−0.141	−0.974	−0.210	0.005
Ho	−0.967	−0.240	−0.046	−0.961	−0.267	0.027
Er	−0.962	−0.263	−0.022	−0.941	−0.333	0.029
Tm	−0.930	−0.352	0.035	−0.921	−0.385	0.015
Yb	−0.924	−0.366	0.075	−0.899	−0.432	−0.004
Lu	−0.907	−0.375	0.137	−0.891	−0.438	0.016
Eigenvalue	12.6	1.07	0.180	12.1	1.64	0.154
% variance explained	90.2	7.67	1.28	86.5	11.7	1.10
Cumulative % variance	90.2	97.9	99.1	86.5	98.2	99.3
<i>Floodplain sediment</i>						
La	−0.948	0.289	0.070	−0.946	0.303	0.060
Ce	−0.963	0.240	0.046	−0.881	0.437	0.132
Pr	−0.968	0.238	0.048	−0.955	0.293	0.027
Nd	−0.958	0.269	0.056	−0.964	0.255	0.000
Sm	−0.980	0.164	0.038	−0.984	0.153	−0.029
Eu	−0.934	0.280	−0.062	−0.945	0.138	−0.283
Gd	−0.987	0.032	−0.066	−0.990	0.105	−0.018
Tb	−0.985	−0.039	−0.133	−0.996	−0.016	−0.014
Dy	−0.958	−0.158	−0.184	−0.986	−0.154	0.008
Ho	−0.963	−0.191	−0.132	−0.976	−0.213	0.015
Er	−0.962	−0.237	−0.045	−0.956	−0.282	0.033
Tm	−0.933	−0.295	0.073	−0.951	−0.299	0.055
Yb	−0.937	−0.316	0.096	−0.935	−0.350	0.019
Lu	−0.921	−0.296	0.212	−0.936	−0.348	0.005
Eigenvalue	12.8	0.771	0.152	12.8	0.968	0.108

**Table 4 (continued)**

Element	Italy			Sweden		
	PC1	PC2	PC3	PC1	PC2	PC3
<i>Floodplain sediment</i>						
% variance explained	91.6	5.51	1.09	91.7	6.92	0.773
Cumulative % variance	91.6	97.1	98.2	91.7	98.6	99.4
<i>Stream water</i>						
La	−0.937	0.280	0.001	−0.976	0.185	0.015
Ce	−0.923	0.310	−0.004	−0.960	0.220	0.098
Pr	−0.942	0.297	−0.017	−0.987	0.143	−0.042
Nd	−0.948	0.294	−0.024	−0.989	0.121	−0.055
Sm	−0.932	0.328	−0.036	−0.992	0.087	−0.065
Eu	−0.774	0.366	−0.348	−0.968	0.051	0.204
Gd	−0.775	0.263	0.520	−0.995	0.045	−0.067
Tb	−0.951	0.236	−0.008	−0.996	0.034	−0.051
Dy	−0.986	0.064	−0.027	−0.995	−0.045	−0.068
Ho	−0.944	−0.303	−0.009	−0.995	−0.082	−0.038
Er	−0.857	−0.509	−0.003	−0.990	−0.137	−0.010
Tm	−0.730	−0.681	−0.001	−0.982	−0.181	0.017
Yb	−0.641	−0.763	−0.018	−0.979	−0.198	0.031
Lu	−0.604	−0.793	0.001	−0.966	−0.242	0.041
Eigenvalue	10.4	2.75	0.395	13.5	0.289	0.077
% variance explained	74.3	19.6	2.82	96.7	2.06	0.548
Cumulative % variance	74.3	93.9	96.7	96.7	98.8	99.3

scale of the present investigation, anthropic activities (industry, waste disposal, etc.) have little influence on the REE distribution.

Data from Sweden show that REE content in soil is strongly correlated to pegmatitic rock and/or mineralisation. A peculiar difference between the two countries is the REE enrichment in topsoil and subsoil, which is completely reversed. In Italy, maximum enrichment is recorded in topsoil, and in Sweden in subsoil. The negative ratio topsoil/subsoil, typical of Swedish soils, testifies an overall leaching of REEs content in clay minerals during pedogenesis, which is more effective in organic matter-rich clay acidic soil (as it is the case of Fennoscandia soil). Acidity in the soil of northern Europe is related both to the overall absence of limestone rocks, and to cold climate (Wilding et al., 1984).

However even in those regions of Italy where the bedrock is not made-up of limestone, but of granitoid crystalline rocks, Variscan carbonate-poor detrital sediments, or alkaline volcanic rocks (see Figs. 1 and 2), and an acidic soil could be expected, the REE topsoil/subsoil ratio is opposite with respect to Sweden. The results of our study make it possible to argue that climate and growing of coniferous forest are the main factor controlling the leaching of REE in Swedish topsoil. The role of organic matter, in fact, is crucial for the mobility of REE. The soil organic matter has many negatively charged groups per unit dry weight, and a high capacity to adsorb or chelate divalent and trivalent cations (Miao et al., 2008). Podzol-like Swedish soil shows a sharp transition between the decimetre-thick humus made topmost layer and the underlying mineral soil layer. Italian soil, on the contrary, has generally a thin highly decomposed well aggregated organic matter layer with rubber fibre content. REE concentration in Italian topsoil with respect to subsoil can be related to biological effects at the interface between the mineral soil and organic matter. In young active volcanic areas, such as the Roman–Neapolitan province, the possibility of new input of REE rich glass fragments to the topmost part of the soil, mostly wind-driven, cannot be ignored.

Another difference emerging between the two countries is the highest percentage of soil developed on in-situ rocks in Italy. In Italy, apart from few cases, mainly located in the Alpine pediment, where the soil developed on clastic sediments from weathering and degradation of granitic or dolomitic rocks making-up the mountain chain, most soil is developed on in-situ rock basement, so there is a close relationship between REE content of parent rock and soil, reflected by the correlation between REE distribution and the geological nature of the underlying rocks. In Sweden, there is abundance of soil developed on moraine deposits, which makes it more difficult to

**Table 5**

Summarised results on number and name of clusters based on plots of loadings of REE on PC1, PC2 and PC3.

Media	Country	PC1 versus PC2	PC1 versus PC3	PC2 versus PC3
Topsoil	Italy	2 (LREE and HREE)	2 (Eu and other REEs)	2 (Eu and other REEs)
Topsoil	Sweden	2 (LREE and HREE)	3 (Eu, Ce and other REEs)	3 (Eu, Ce and other REEs)
Subsoil	Italy	2 (LREE and HREE)	2 (Eu and other REEs)	2 (Eu and other REEs)
Subsoil	Sweden	2 (LREE and HREE)	3 (Eu, Ce and other REEs)	3 (Eu, Ce and other REEs)
Stream sediment	Italy	2 (LREE and HREE)	2 (Eu and other REEs)	2 (Eu and other REEs)
Stream sediment	Sweden	2 (LREE and HREE)	3 (Eu, Ce and other REEs)	2 (Eu and other REEs)
Floodplain sediment	Italy	2 (LREE and HREE)	2 (Lu and other REEs)	3 (Eu, LREE and HREE)
Floodplain sediment	Sweden	3 (Ce, LREE and HREE)	3 (Eu, Ce and other REEs)	2 (Eu and other REEs)
Stream waters	Italy	3 (LREE, EU-Gd, and HREE)	3 (Gd, Eu, and other REEs)	3 (Gd, Eu, and other REEs)
Stream waters	Sweden	2 (LREE and HREE)	2 (Eu and other REEs)	2 (Eu and other REEs)

identify a direct relationship between REE distribution in soil and source rocks.

Stream sediment, both in Italy and Sweden, reflects the geological setting of the river catchment basins. In Italy, there is a more complex patchwork of REE distribution in stream sediment, possibly in response to the more varied geological setting and to the still highly active erosion processes on mountain terrains, due to the “young” geotectonic evolution of the country. PCA analysis on Italian stream sediment samples pointed out the different behaviours of Lu with respect to other REEs, for which we hypothesise the possible effects of anthropic activities. In Sweden, on the contrary, the occurrence of moraine remobilised deposits and mineralised areas play a more distinctive role.

Dispersion patterns of the light REE, compared with the heavy REE, show distinct differences in the south-eastern part of Sweden. Here, the light REE are enriched where river beds have high Al and K concentrations and are clay-rich. The heavy REE do not follow this trend except in Blekinge. Both light and heavy REE are anomalous (positive) in most part of the Caledonides. In Lapland, where REE mineralisation occurs, the river beds have high REE concentrations. High REEs dominate over light REEs east of the Kiruna mining district.

In Italy, floodplain sediments seem to mimic the REE distribution pattern in other solid media, with the exception of some anomalies for Lu and Dy, possibly related to an external input due to alteration that enhances the REE content of the clay-rich sediments. Some accessory minerals in granite containing heavy REE, as doverite – an yttrium fluorocarbonate, and volcanic glass (Christidis, 1998) are, in fact, more prone to chemical weathering and in warm and moist climates, as it is the case of Italy, they tend to be altered and the HREE are fixed onto clay minerals in the advanced stages of chemical weathering (Bao and Zhao, 2008).

Sweden has high REE concentrations in stream water and their median values are generally higher compared with the rest of Europe (De Vos et al., 2006; Salminen et al., 2005). The main source of such enrichment in stream water is the felsic rocks of the Fennoscandian Shield, which also explains the high acidity of stream water. Owing to the abundance of particulate and colloid-sized material they tend to be enriched, especially in the light REE (Åström and Corin, 2003). Heavy REE form more stable complexes, like carbonate and fluoride, than LREE. High REE contents in the stream water in the southern part of Sweden dominate the dispersion patterns. The low pH in the stream water and the high concentrations of dissolved organic matter (DOC) are characteristic in the areas of Småland and Hälsingland. Mineralised areas are generally not clearly discernible, though weak anomalies in Lapland (heavy REE) and along the coast of Västerbotten (Varuträsk, light REE) may reflect mineralisation.

In this regard, the opposite behaviour in terms of REE content can be explained by exogenic factors in the two countries. In Sweden, cold climate and high acidity linked to Nordic vegetation and mostly low topography, cause REE enrichment in stream water. Whereas, in Italy, stream water is more mineralised, its pH is higher, and the zone of contribution to surface water, both in the pre-Alpine and Apennine region, are mainly made of limestone and dolomitic rocks, causing the overall

low REE content in stream water. In Italy anomalies occur only in Latium-Neapolitan volcanic areas and at the Vulture volcano, where the mixing of stream water with water from shallow water tables, residing in REE-rich volcanic rocks, could be the source of REE anomalous contents.

## 8. Conclusive remarks

Both in Italy and Sweden, solid media show a REE content inherited from the local bedrock, and surficial processes acted locally to increase or reduce these contents. Anthropogenic contribution to REE concentrations in solid media is not evident, at least at the scale of the FOREGS database, with the exception of few examples found in Italian stream water and stream sediment samples.

Unlike Sweden, in Italy extraction of REE from alkali-granite is not economically feasible due to the narrow extent of the outcrops. Associated placer-type deposits, where REE-bearing minerals, such as bastnaesite and monazite can be concentrated along with other heavy minerals, are almost absent in Italy, mainly due to the temperate climate that prevents the extreme effects of erosion. Vice versa, our results show that in many Italian areas REE concentrations in soil and sediments is notably high, particularly in soil developed on alkali volcanic products. In these areas, embedded within pyroclastic sequences, huge volumes of fossil soil (palaeosol) are available, which formed on bedrocks and under climatic conditions similar to those of the present soil. Because of this, our results allow us to quite confidently hypothesise that the palaeosol REE content is comparable to that of present soil.

A particular type of REE deposit, the ion-absorption type, is formed by the leaching of REE from seemingly common igneous rocks and fixing the elements onto clay in soil (Bao and Zhao, 2008). Some projects are now being carried out in southern China to attempt extraction of REE from clay minerals of the weathered crust of alkali granite (Kazanawa and Kamitani, 2006), and new desorption mechanisms are being tested (Moldoveanu and Papangelakis, 2012). This is one of the ways to cope with the pollution linked to the extraction of REE from heavy minerals, such as monazite, which involves a huge production of radioactive waste. Italian palaeosol, developed on alkaline volcanic products could be further investigated to assess the potential extraction of REE formed by ion-adsorption processes. Future research should be focused on locating new REE deposits, and to develop less pollutant exploitation methods, in response to the increase REE demand on the world market. Development of new technological applications and commercial use of REEs should coincide with increased research aimed at the protection of the environment and human health.

## Acknowledgement

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## Appendix A. Supplementary data

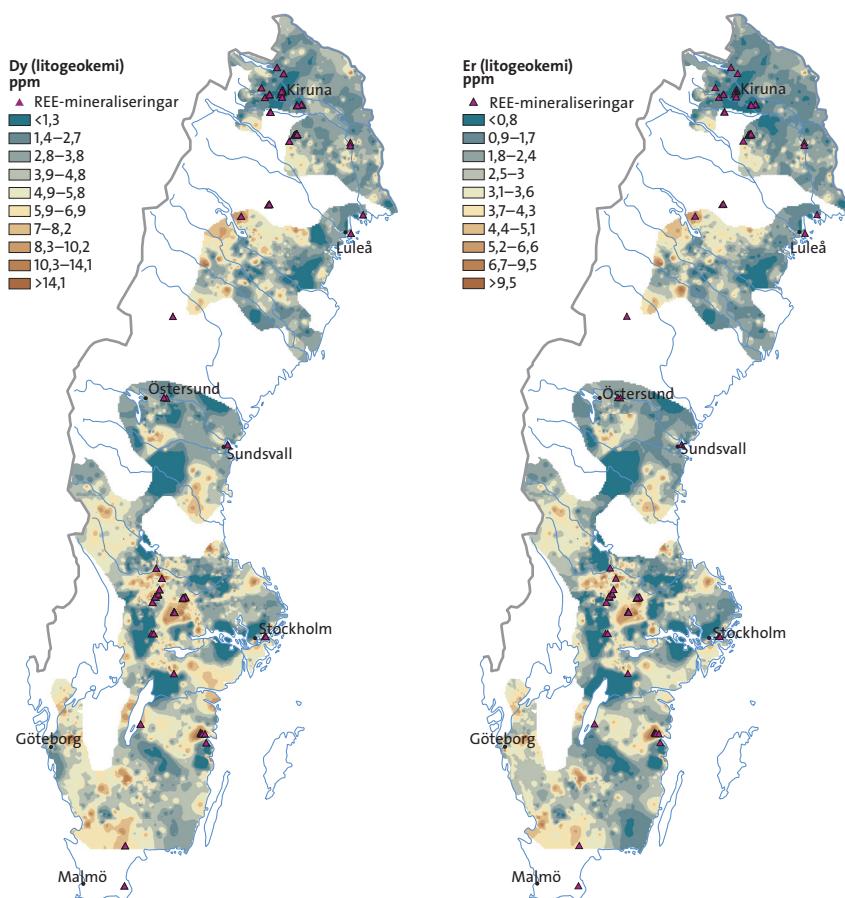
Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.gexplo.2012.12.008>.

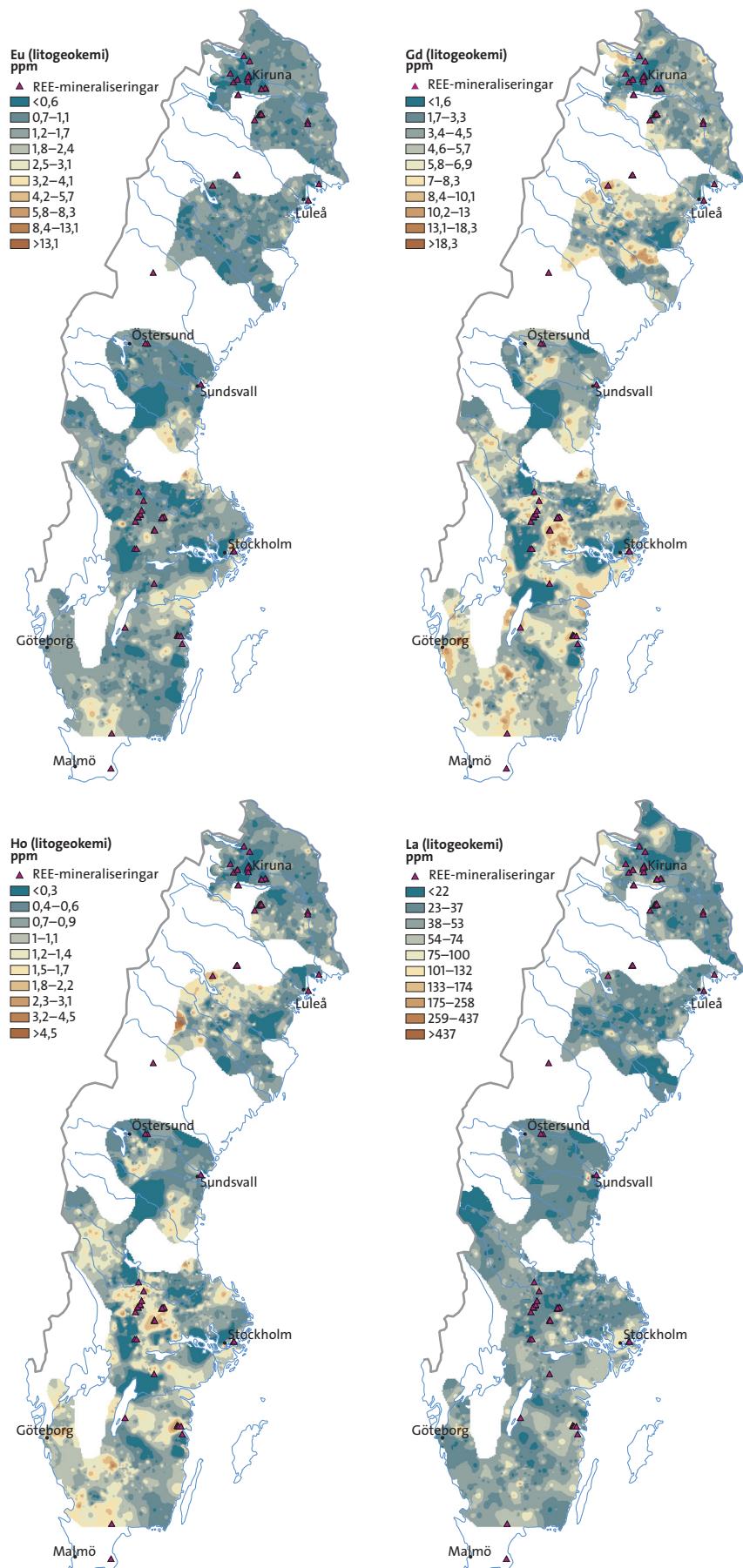
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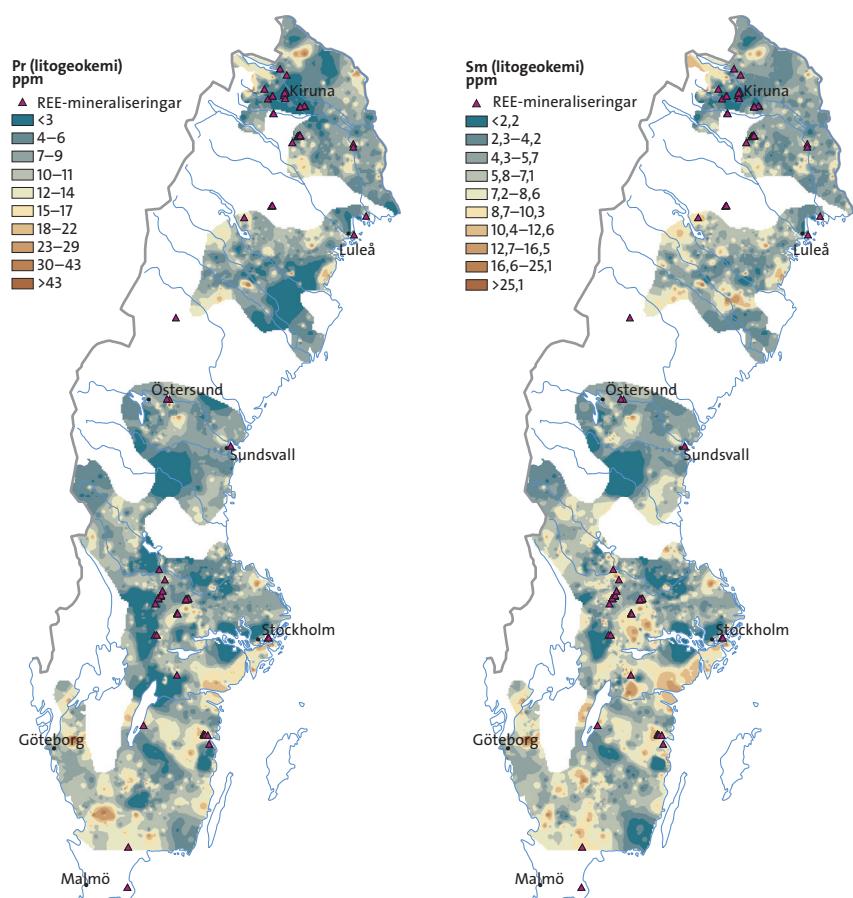
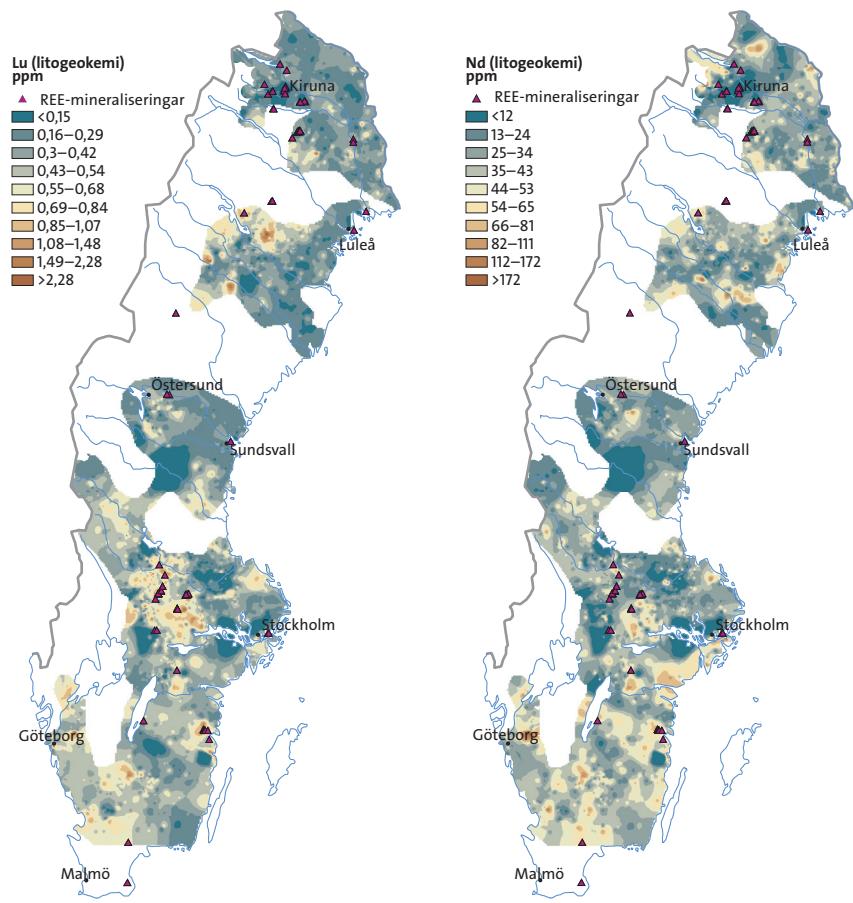
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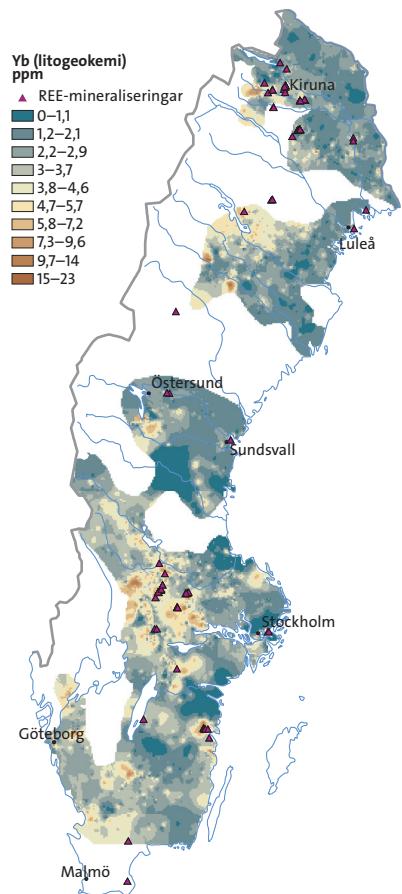
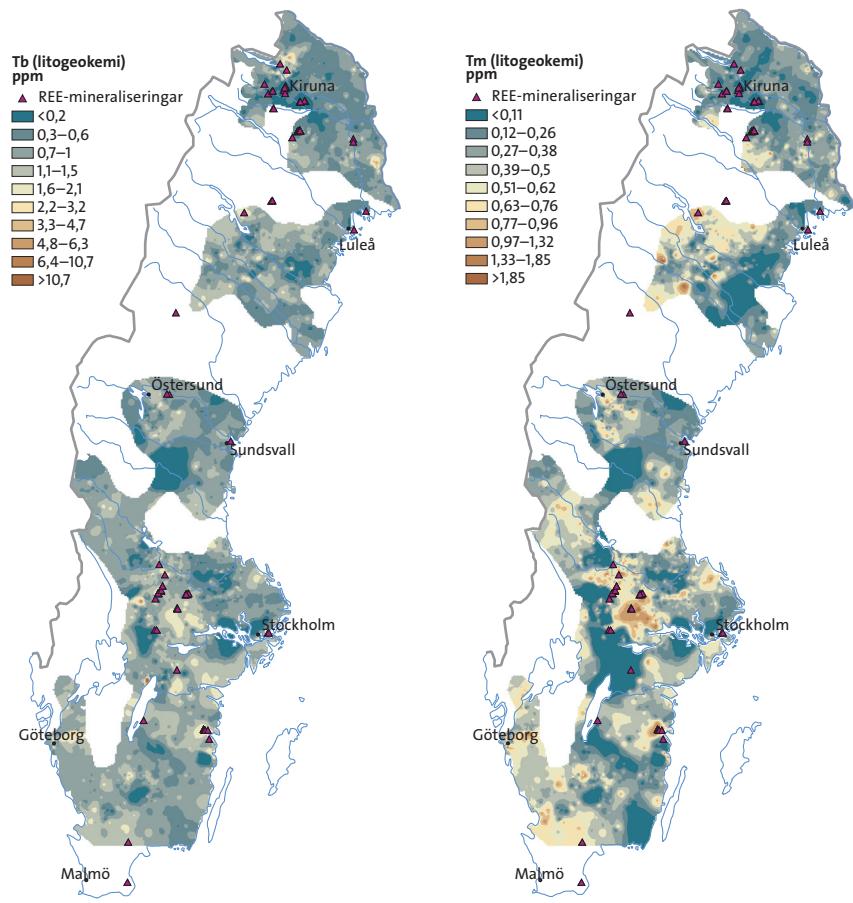
## BILAGA 2. LITOGEOKEMiska KARTOR ÖVER SÄLLSYNTA JORDARTSMETALLER

Kartorna visar spridningsmönster för de sällsynta jordartsmetallerna dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lantan (La), lutetium, (Lu), neodym (Nd), praseodym (Pr), samarium (Sm), terbium (Tb), tulium (Tm) och ytterbium (Yb) i berggrunden, samt kända mineraliseringar. Antal prov: 5 761. Analyser av totalhalter i malt prov med ICP-MS. Källa: SGUs litogeokemiska databas.



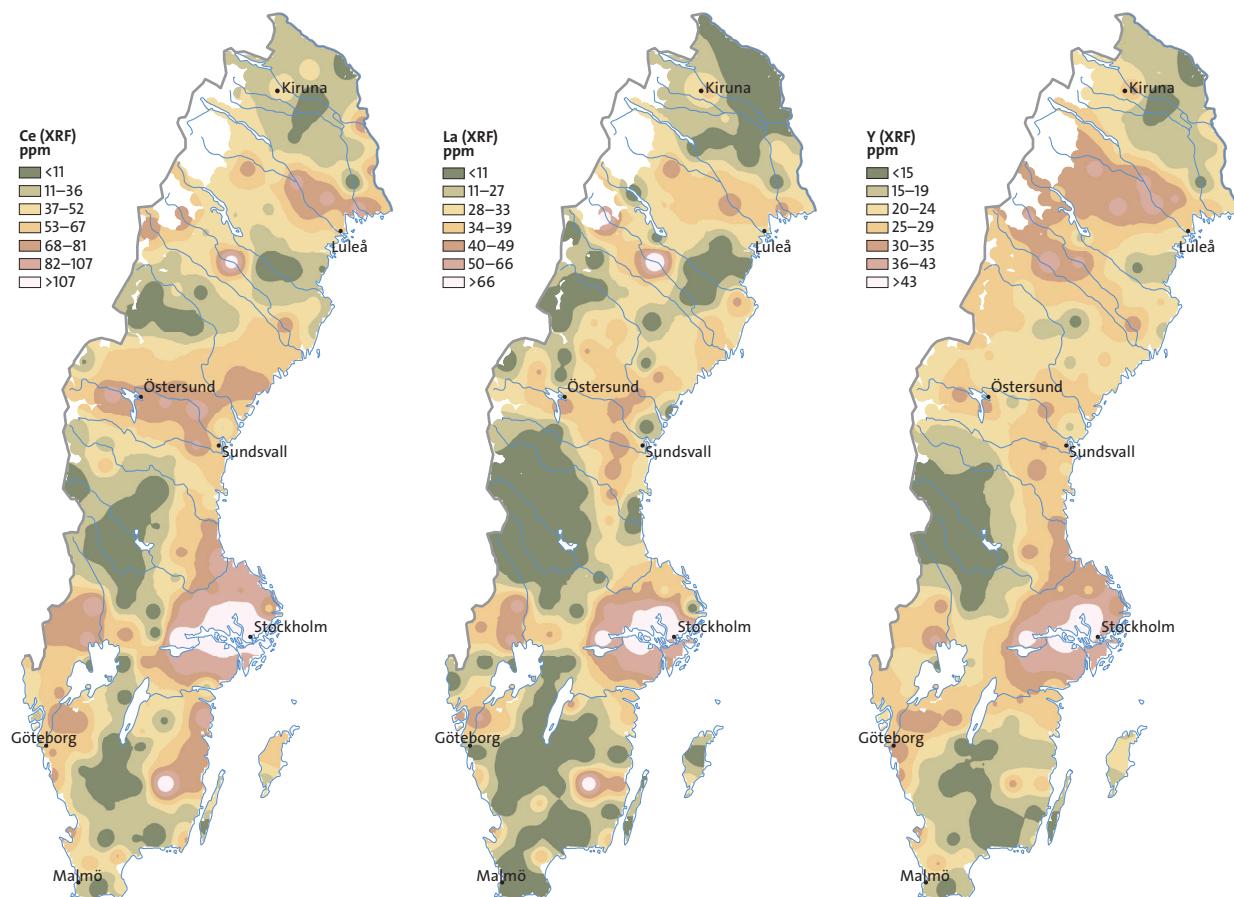






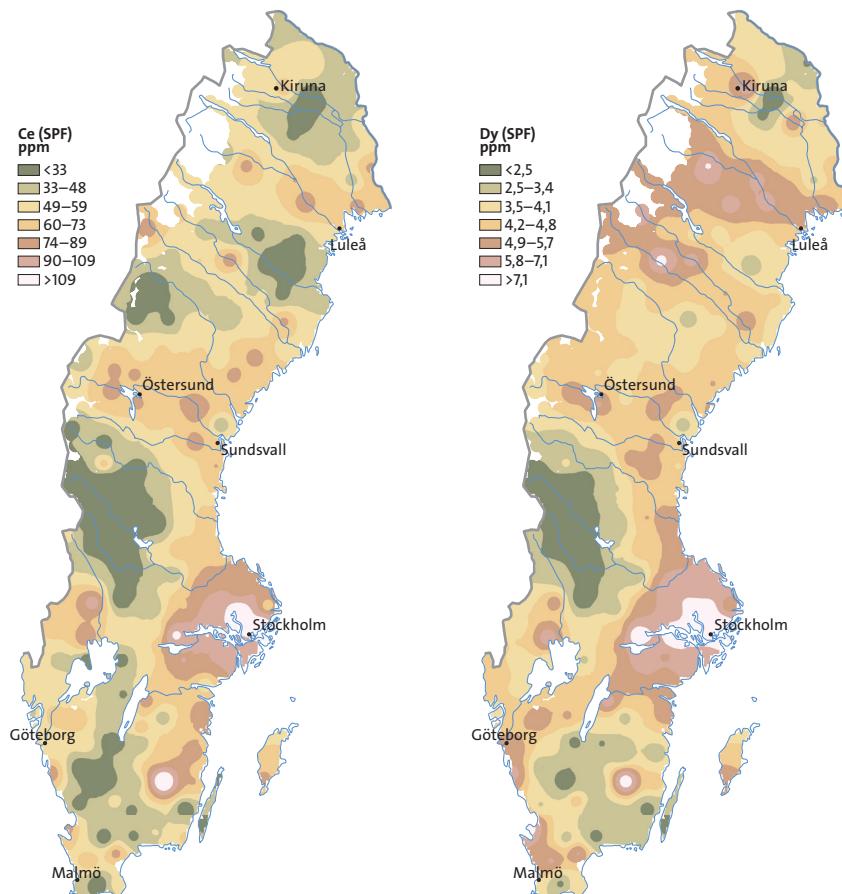
### BILAGA 3. Geokemiska kartor över totalhalter av sällsynta jordartsmetaller i åkermark, analyserade med XRF

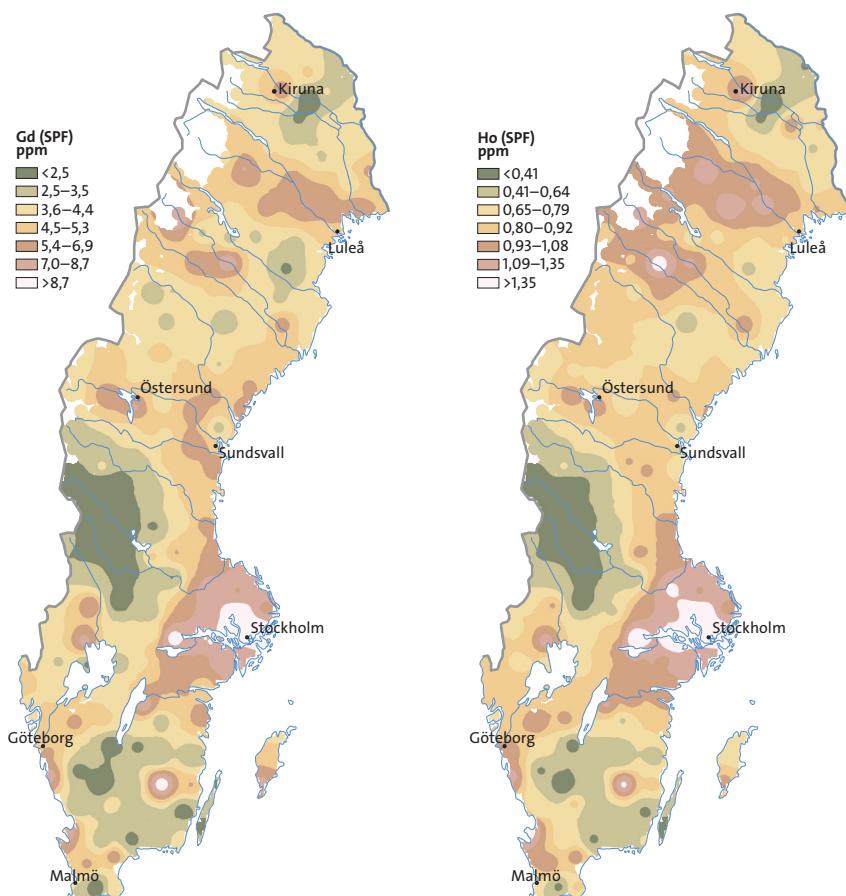
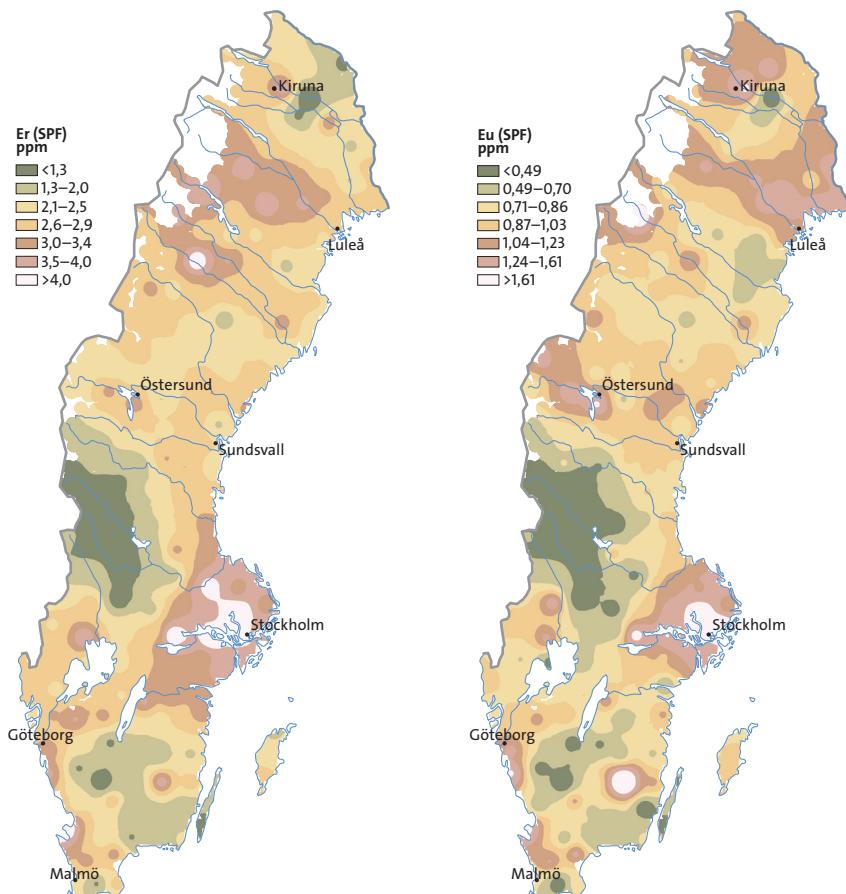
Cerium (Ce), lantan (La) och yttrium (Y) i åkermark (fraktion <2mm). Antal prov: 174. Analys-metod: totalhalter med röntgenfluorescens (XRF). Källa: GEMAS databas.

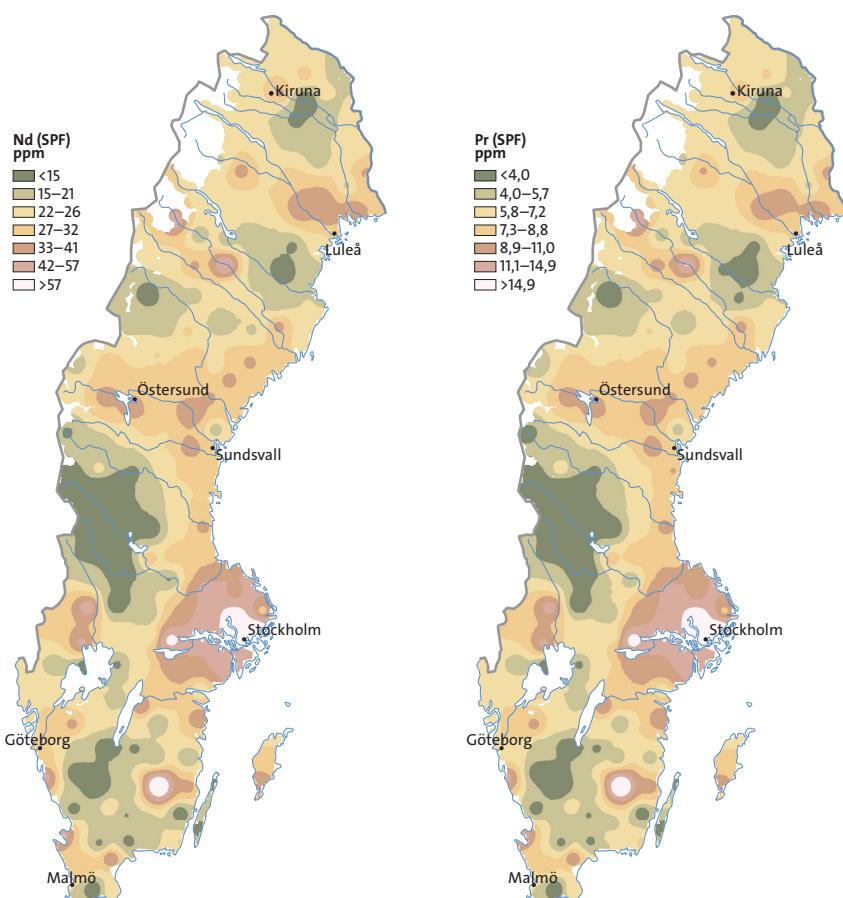
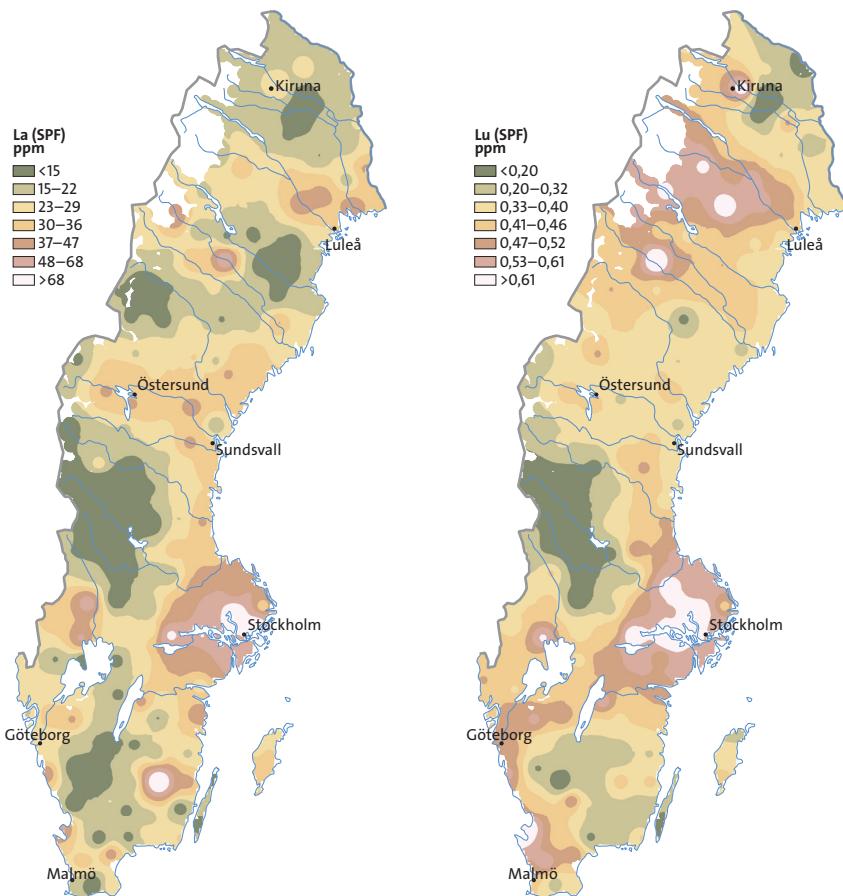


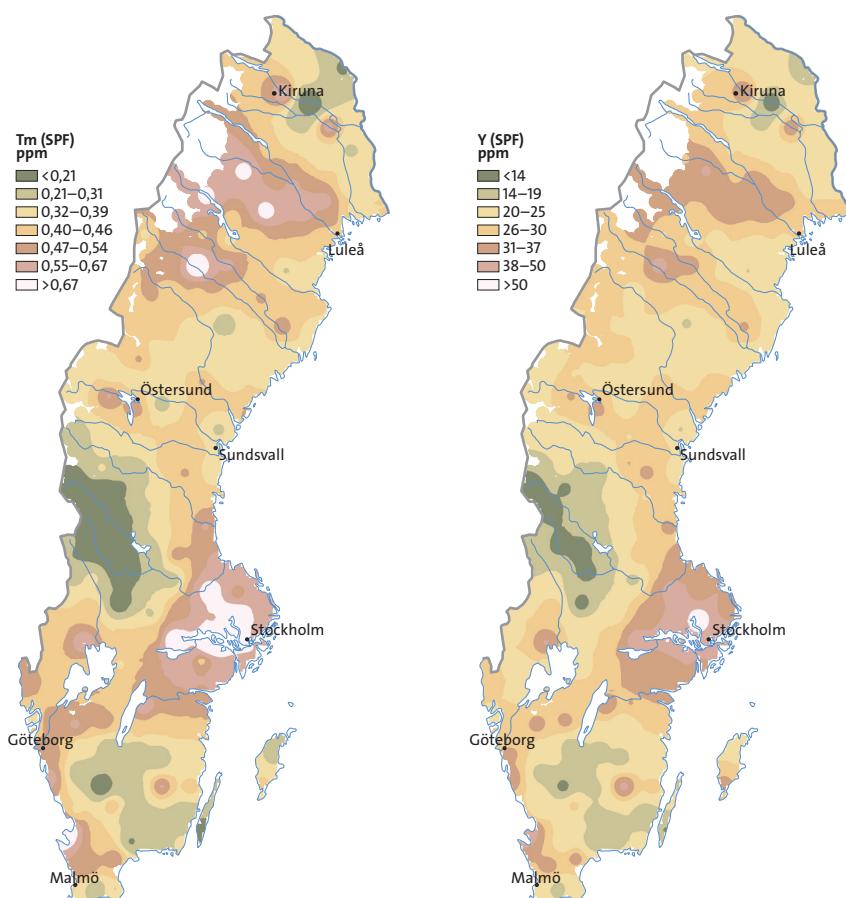
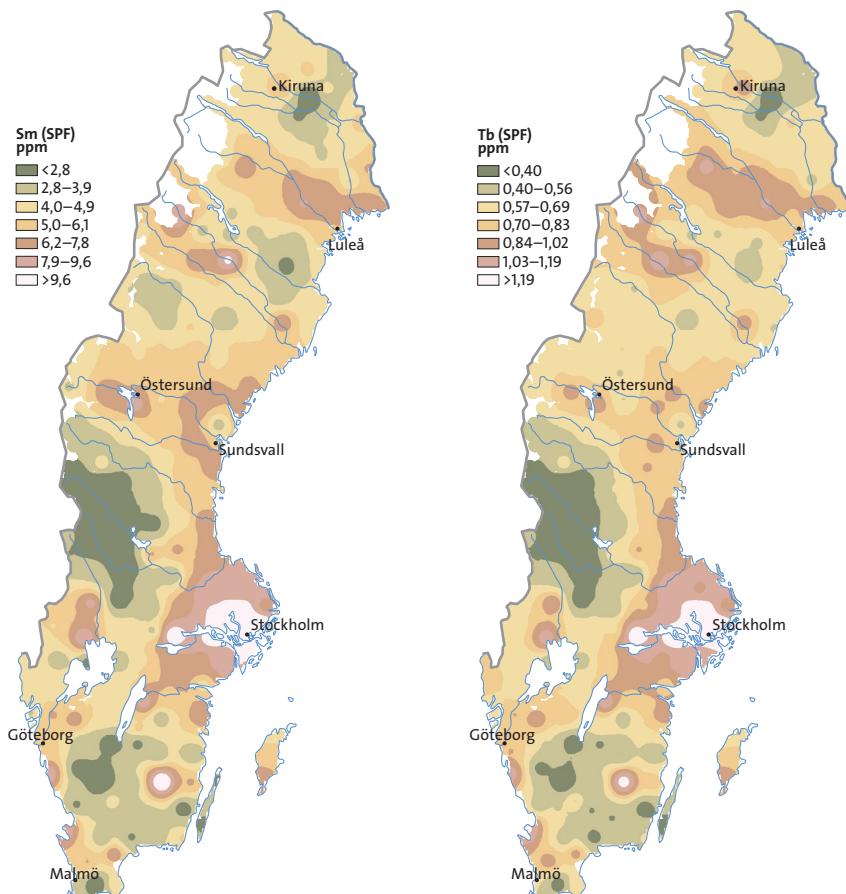
#### BILAGA 4. Geokemiska kartor över totalhalter av sällsynta jordartsmetaller i åkermark, analyserade med natriumperoxid

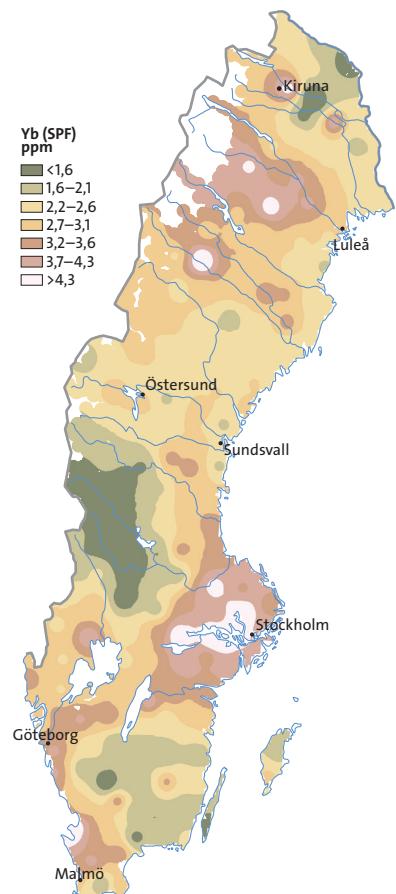
Cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lantan (La), lutetium, (Lu), neodym (Nd), praseodym (Pr), samarium (Sm), terbium (Tb), tulium (Tm), yttrium (Y) och ytterbium (Yb) i åkermark (fraktion <2 mm). Antal prov: 174.  
Analysmetod: totalhalter efter uppslutning med natriumperoxid (sodium peroxide fusion, SPF).  
Källa: SGU.





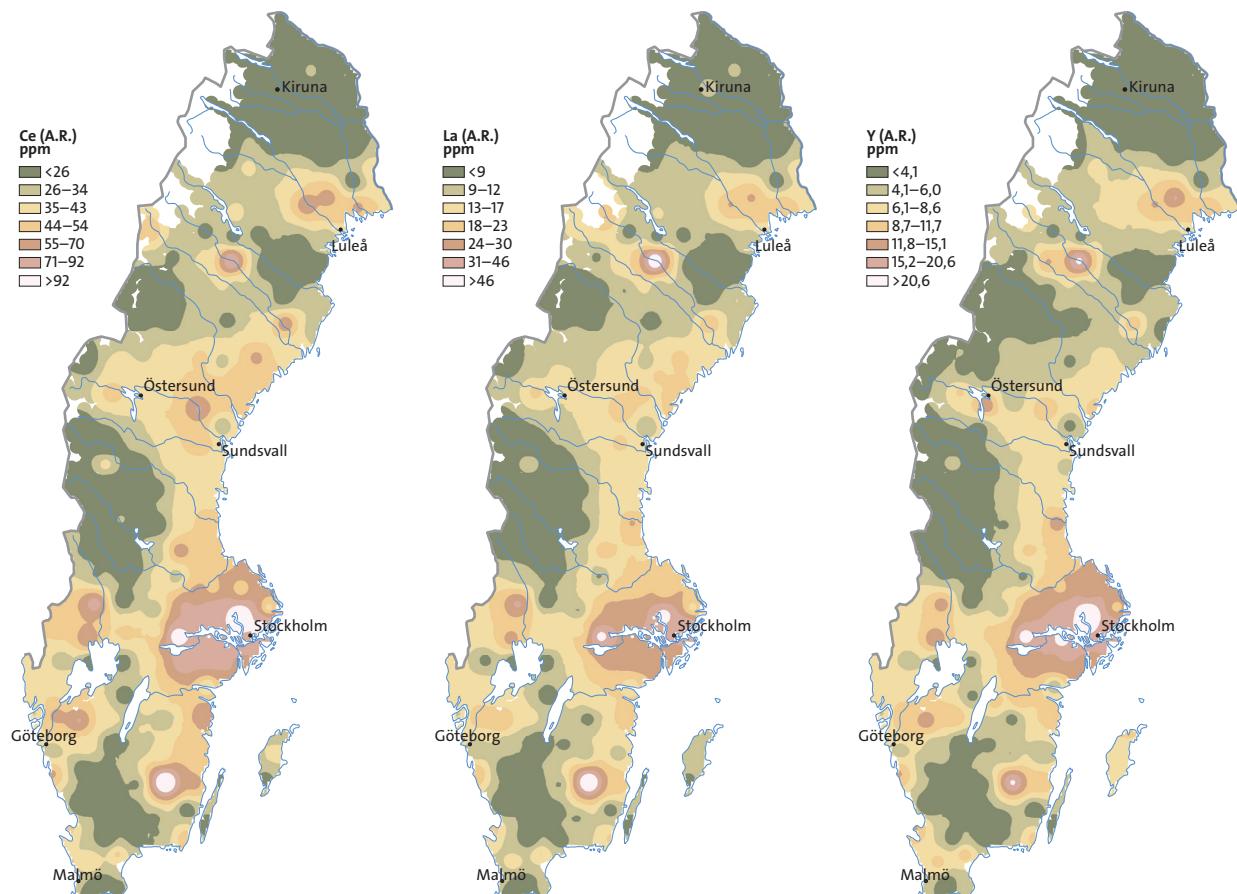






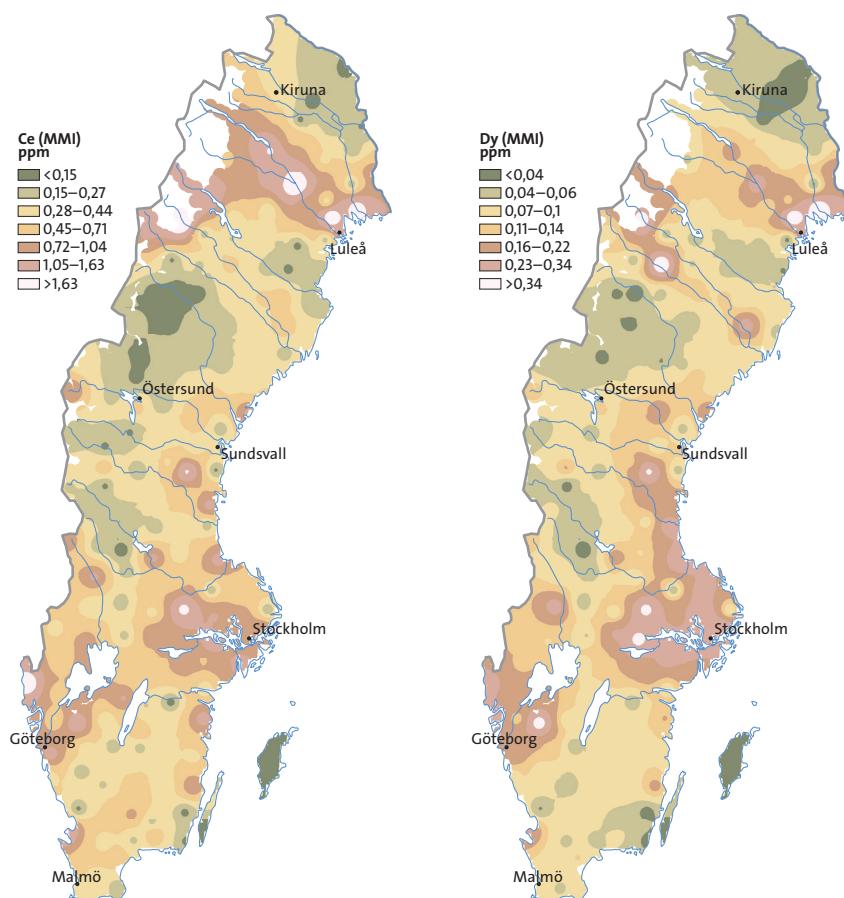
## BILAGA 5. Geokemiska kartor över sällsynta jordartsmetaller i åkermark, analyserade efter kungsvattenlakning

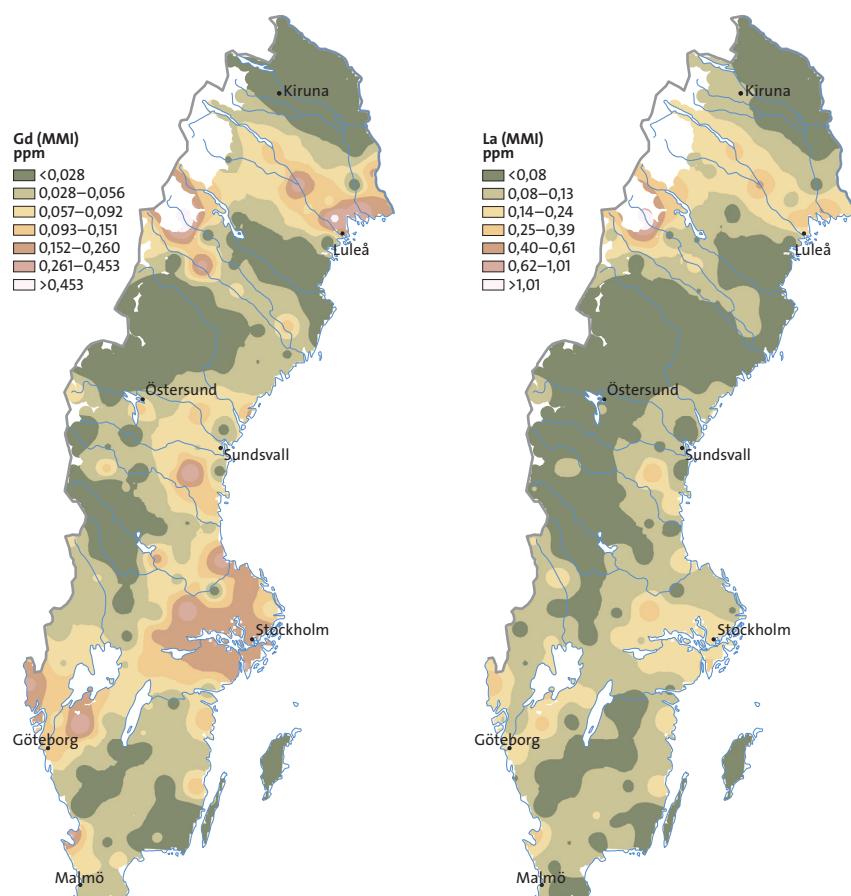
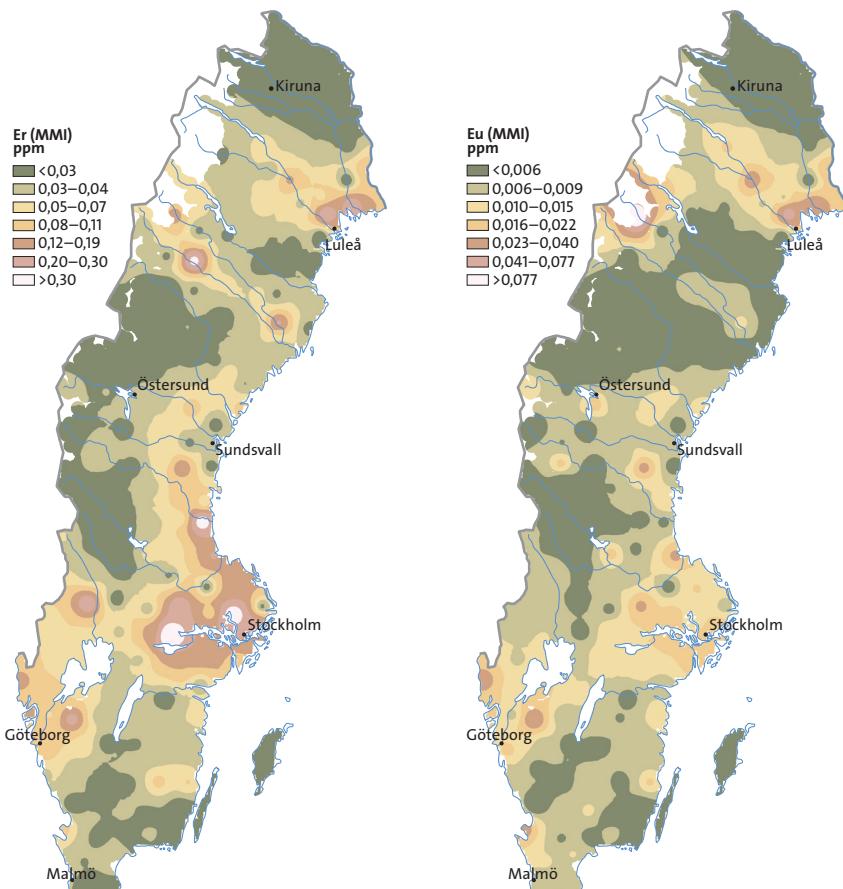
Cerium (Ce), lantan (La) och yttrium (Y) i åkermark (fraktion <2 mm). Antal prov: 174.  
Analysmetod: kungsvattenlakning (AR) och ICP-MS. Källa: GEMAS databas.

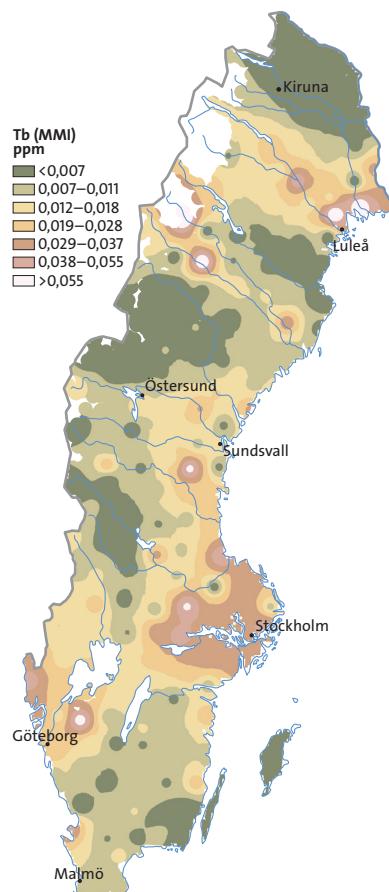
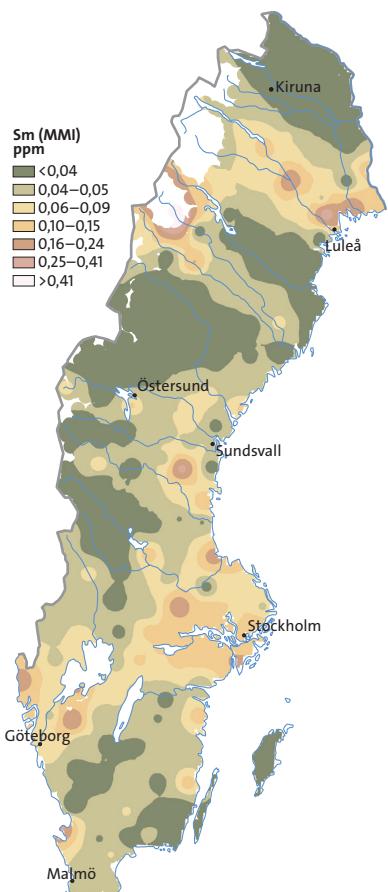
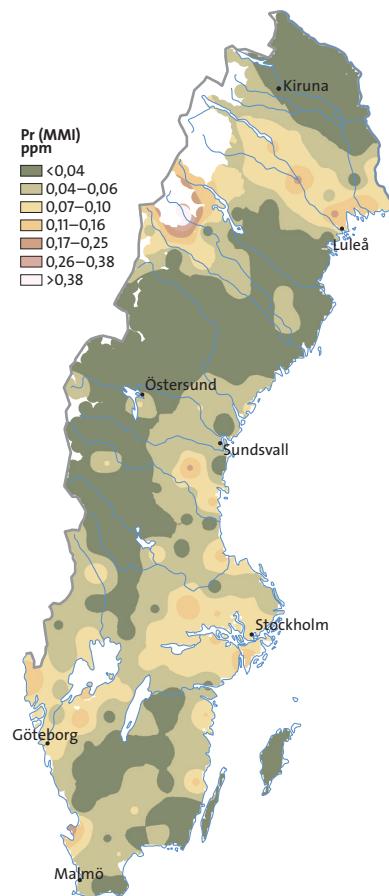
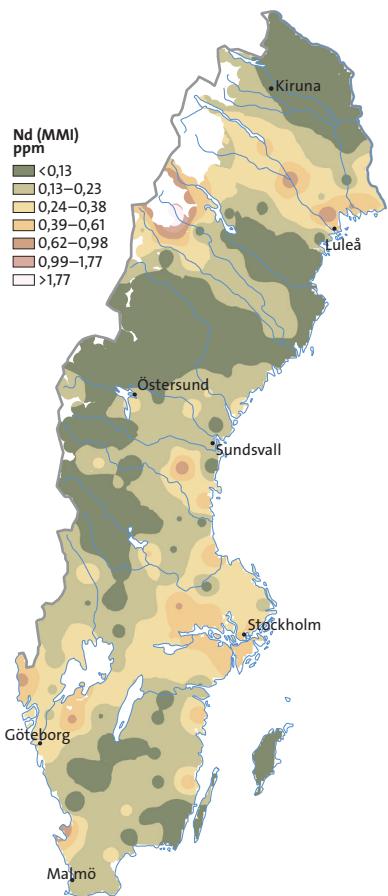


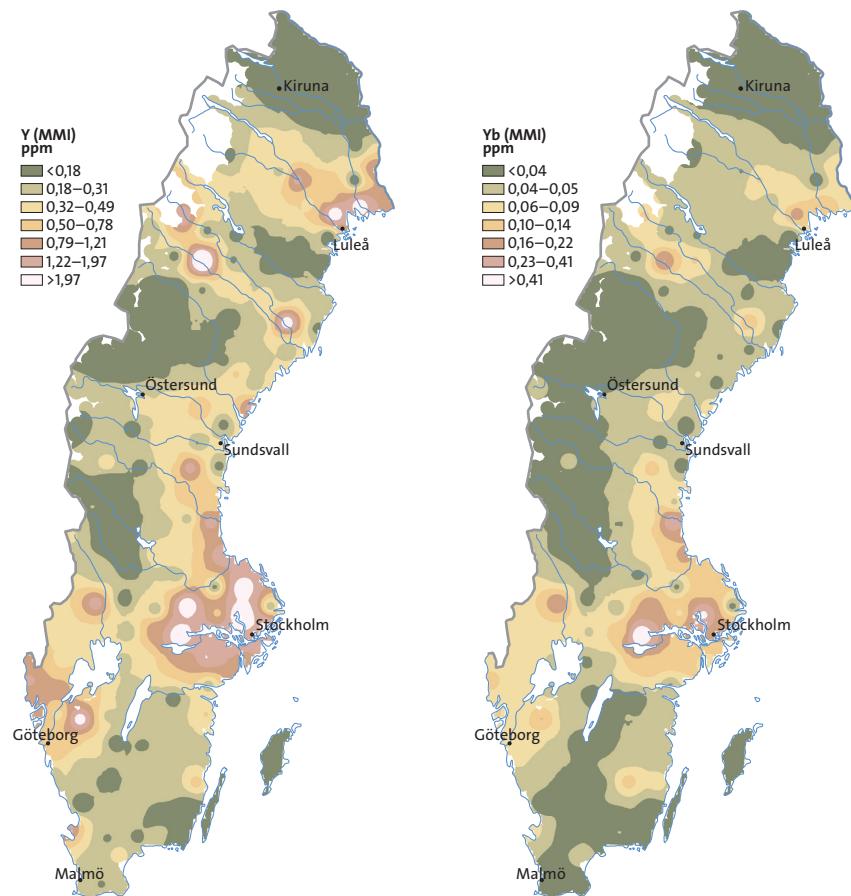
## BILAGA 6. Geokemiska kartor över sällsynta jordartsmetallers mobila metalljoner i åkermark

Cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), lantan (La), neodym (Nd), praseodym (Pr), samarium (Sm), terbium (Tb), yttrium (Y) och ytterbium (Yb) i åkermark (fraktion <2 mm). Antal prov: 174. Analysmetod: extraktion med MMI® och ICP-MS.  
Källa: GEMAS databas.









## BILAGA 7. Geokemiska kartor över sällsynta jordartsmetaller i morän analyserade efter kungsvattenlakning

Cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lutetium, (Lu), neodym (Nd), praseodym (Pr), samarium (Sm), terbium (Tb), tulium (Tm) och ytterbium (Yb) i morän (fraktion <0,063 mm). Antal prov: 2 578. Analysmetod: kungsvattenlakning (AR) och ICP-MS. Källa: SGU (GAOS).

