

Geochemical mapping at European scale - the GEMAS-project

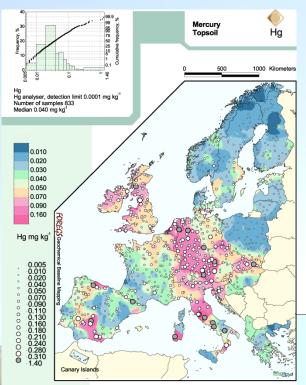


23 August 2013, Berlin, Germany





International Workshop on "Groundwater Systems.



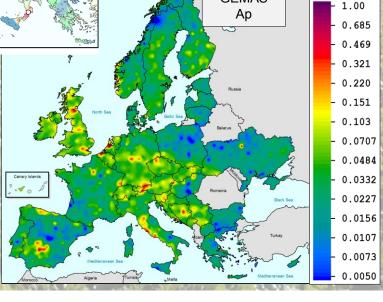
FOREGS Geochemical Atlas of Europe

Sample materials: surface water, stream sediment, topsoil (0 - 20 cm), overbank sediment, soil C-horizon, humus

provide a good first impression of the background in Europe

However, missing: some important soil properties and a sampling according to land use

Hg (mg/kg)



GEMAS

REACH requires:

- the sample depth of 0 20 cm for arable soil and of 0 - 10 cm for grazing land soil
- risk assessment according to land use
- knowledge about soil quality at the European scale



(from Salminen et al., 2005)

EuroGeoSurveys/

cooperation project:

GEMAS Atlas

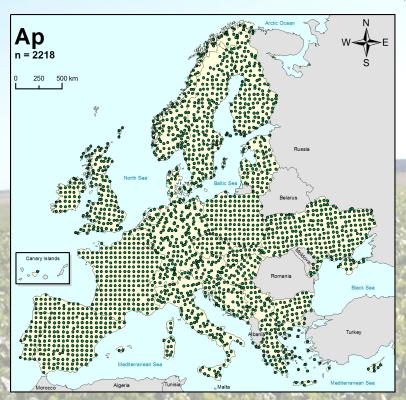
Eurometaux

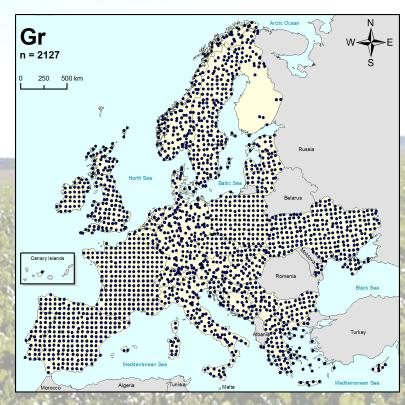


Sample distribution in Europe

Agricultural soils (Ap, 0-20 cm) Grazing land soils (Gr, 0-10 cm)

2 samples at 1 site/2500 km², collected during 2008; 33 European countries (with exception of Malta, Albania and Romania); 5.6 mill. km²





> It was strived to collect both soil samples in dose proximity, but depending on land use in any one area, distance up to few km between the two sample plots were not uncommon.





Agricultural soil, Germany, site 18



- > app. 15 km southwest of Hamburg
- podzol on tills and boulder clay







Analytical program of chemical elements and general soil properties

- > Sample preparation: air dried, sieved, homogenized and split to subsamples
- Aqua regia extraction on 15 g aliquots (ICP-MS): 53 elements
 Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In,
 K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta,
 Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr
- ➤ Total element concentrations (XRF): 42 parameter SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, SO₃, Cl, F, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn, Zr and LOI (Loss On Ignition)
- ➤ MMI (mobile metal ion) extraction on 50 g aliquots: 56 elements
- > Pb-isotopes (Ap samples); Sr-isotopes (Gr samples)
- > pH (in a 0.01 M CaCl₂ solution), TOC (total organic carbon), TC, TS
- > CEC (cation exchange capacity, by silver-thiourea method)
- > K_d values for the elements Ag, B, Co, Cu, Mo, Mn, Ni, Pb, Sb, Se, Sn, Te, V, and Zn
- > PSD analysis (800 Ap and Gr samples) and MIR spectroscopy





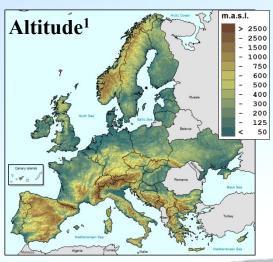
Quality control

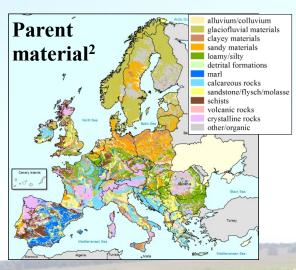
- > a randomisation of all samples before sending them to the analytical laboratory,
- > the collection of field duplicates taken at a rate of 1 duplicate sample in 20 samples,
- > an analytical replicate produced from each field duplicate (Thompson and Howarth-plots, analysis of variance),
- ➤ the frequent insertion of project standards (Ap, Gr) at a rate of 1 per 20 samples (for plotting X-charts),
- > the insertion of international reference materials (ORIS, SONE-1) and
- > a proficiency test using the two project standards (23 laboratories from 16 countries).
- > Each parameter was measured in one single laboratory following strict external QC procedures.
- > QC results are documented in three reports (freely available on the internet): Reimann et al. (2009, 2011, 2012)

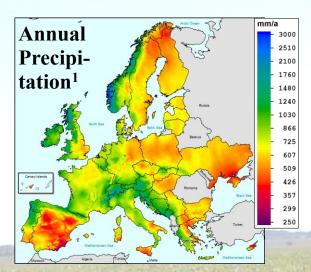


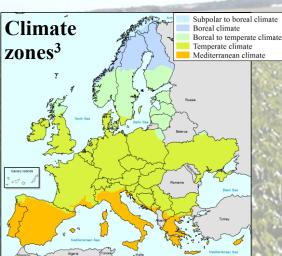


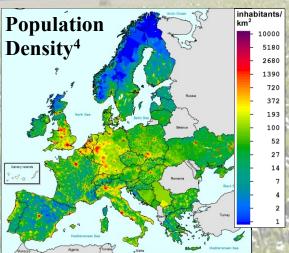
Supporting information for interpretation of geochemical maps











Some further factors that can be expected to influence soil geochemistry at the European scale.

¹ data from www.worldclim.de; ² Günther et al, in press; ³ after Baritz et al., 2005; ⁴ data from CIESIN & CIAT, 2005

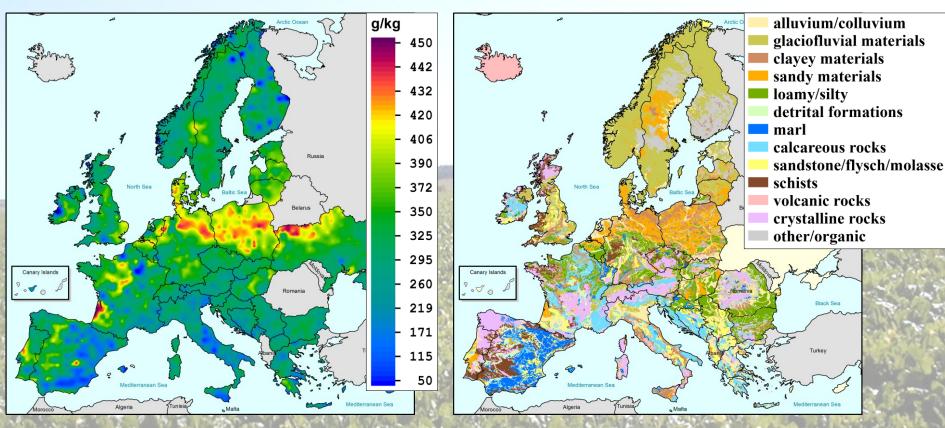




Distribution of total Si concentration in Ap soils of Europe

Agricultural soils (Ap) (0-20 cm, n=2218, XRF)

Soil parent material (Günther et al., in press)



high Si concentrations over the coarse-grained sediments of the last glaciation; also related to the occurrence of coarse-grained sandy soils

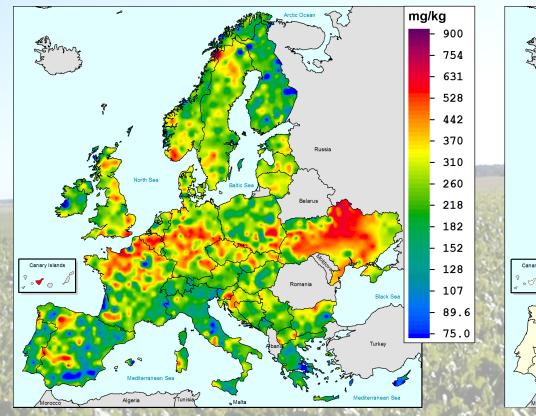


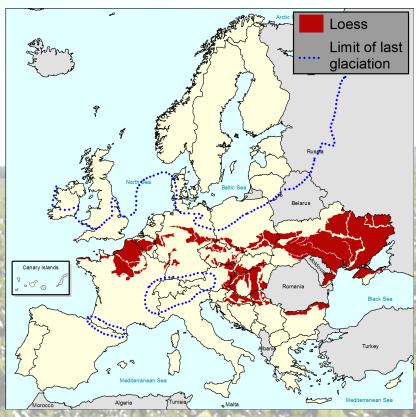


Distribution of total Zr in agricultural soils (Ap) of Europe

Zirconium (Zr) (0-20 cm, n=2219, XRF)

Map of loess deposits in Europe (after Hartwich et al., 2005)





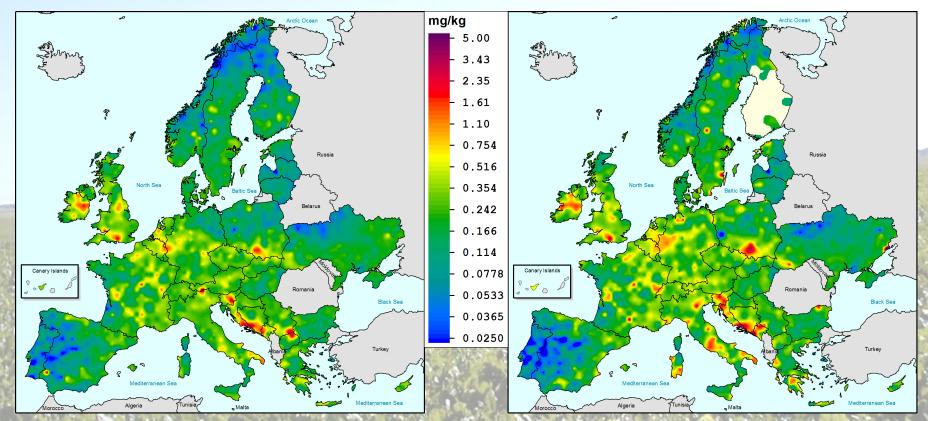
Across Europe, the spatial distribution of high Zr values suggest a much more extensive loess belt across central and eastern Europe as currently mapped and published.





Distribution of Cd in European agricultural and grazing land soils

Agricultural soils (Ap) (0 – 20 cm, n = 2218, AR, ICP-MS) Grazing land soils (Gr) (0 – 10 cm, n = 2127, AR, ICP-MS)



Anomalies are caused by sulphide metal occurrences (e.g. Ireland, UK, Germany, Austria), black shale (e.g. Norway), karst development (e.g. Croatia) and industries (e.g. Poland).

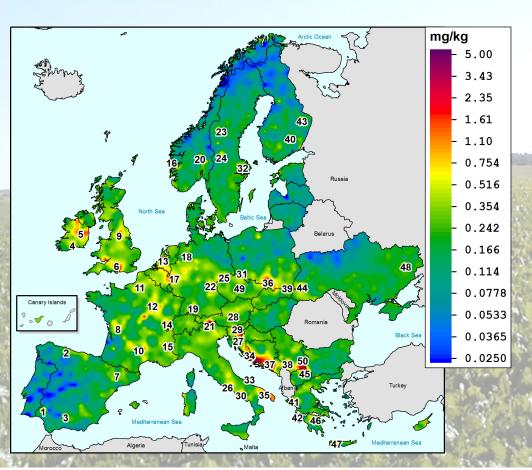




Distribution of Cd in the European agricultural soils (Ap) with numbered anomalies

Cd in agricultural soils

(0-20 cm, n=2218, AR, ICP-MS)



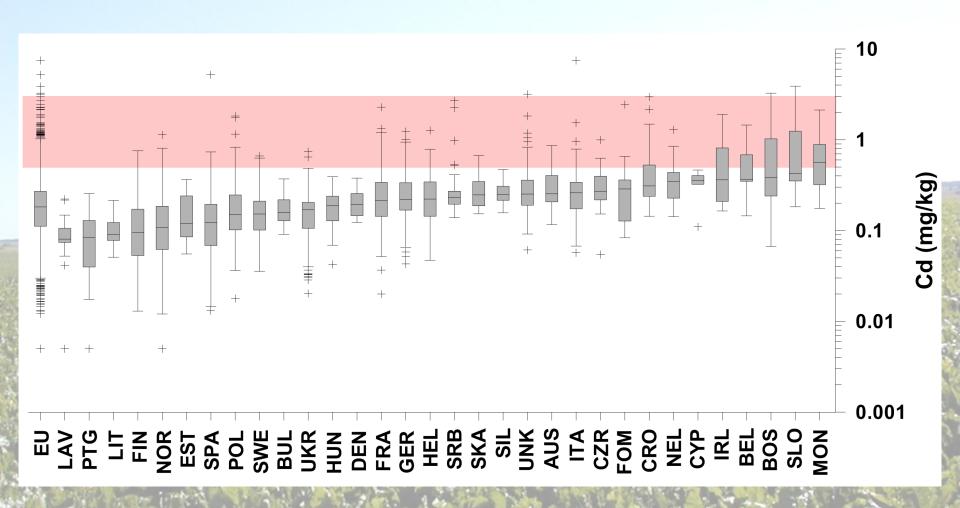
Primary reasons of Cd anomalies

- > Ore deposits and mineralisations: 4, 5, 9, 32, 24, 23, 36, 28, 21, 38, 50, 45, 41, 46, 47, 49, 2, 7, 1, 18, 17, 25, 19, 22, 44
- Geology, parent materials:
 6, 40, 43, 16, 20, 39, 31, 27, 34, 37, 26, 30, 33, 35, 11, 12, 14, 15, 10, 8
- Contamination (industry, agriculture, urban area):
 48, 29, 42, 3, 13





Boxplot comparison of cadmium (Cd) in agricultural soils (Ap) of European countries, with reference to soil limits



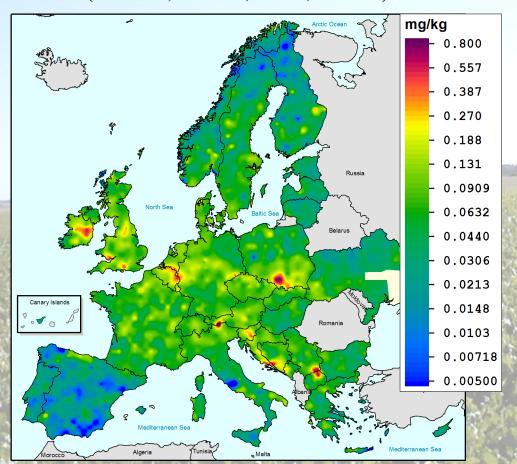




Distribution of Cd (MMI® extraction) in European agricultural soils

Cd in crop land soils

 $(0-20 \text{ cm}, n=2108, \text{MMI}^{\odot}, \text{ICP-MS})$

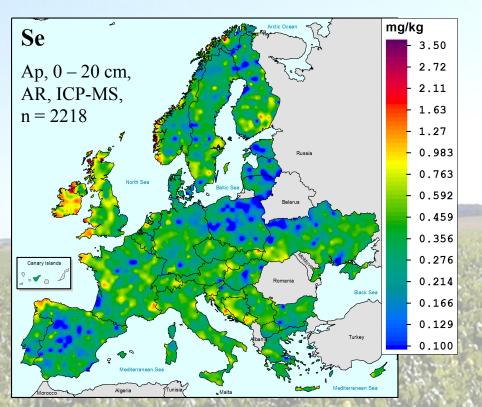


- > about 30 % of the AR extractable Cd
- ➤ the main anomalies caused by mineralisations are mapped in both extractions (AR, MMI®) of Ap samples
- distribution of high and elevated Cd
 values throughout almost of central
 Europe (loess belt) and in the karst areas
 from Croatia to Montenegro
- ➤ location and extend of the anomaly in central Europe suggest an anthropogenic impact on MMI® available Cd concentrations in these soils (land use and input via fertilisers)





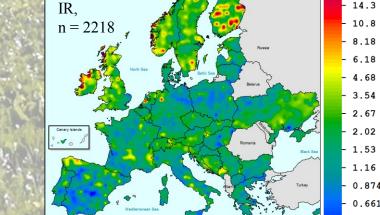
Distribution of selenium (Se) and total organic carbon (TOC) in agricultural soils (Ap) of Europe



- Se anomalies correlate with organic rich soils,
- > strong coastal effect in Ireland, northern Scotland, west coast of Norway, Galicia, Cornwall and Brittany (highest rainfall areas),
- > away from coastal regions, Se anomalies are more related to the geology (e.g. sulphide ore occurrence, black shales, volcanic rocks, red soils etc.).

TOC.

Ap, 0 - 20 cm.



- Effects of the use of Se-fertilizers and supplements in feed are clearly highlighted in southern Sweden and Finland.
 - → strongest influence of climate (and geology)



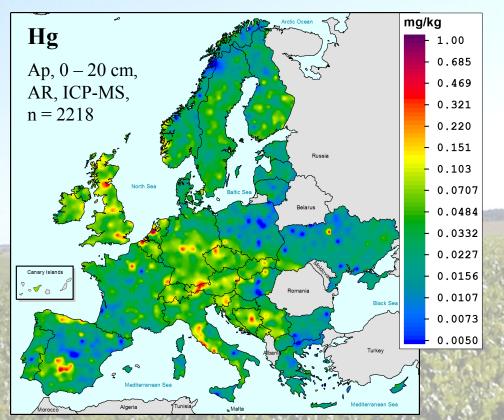


wt%

25.0

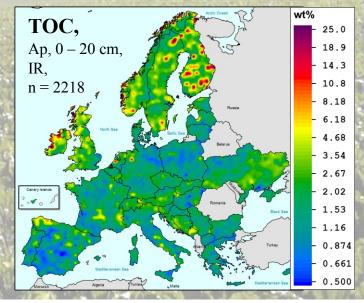
18.9

Distribution of mercury (Hg) and total organic carbon (TOC) in agricultural soils (Ap) of Europe



Anomalies related to:

- mineralisation (ore deposits like Almaden and Monte Amiata)
- geology (border of last glaciation; volcanoes: Phlegrean fields and Vesuvius; several shale areas)
- contamination (e.g. Kiev, London, Dublin, Bilbao, Paris, Rotterdam, Rome)



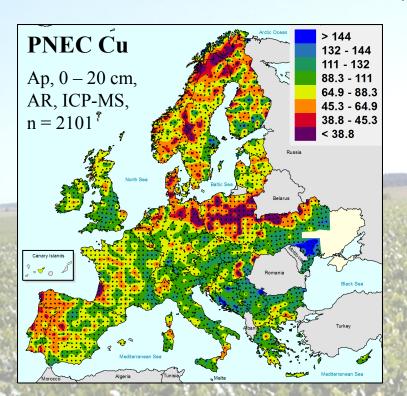
climate and soil formation (large anomaly at the west coast of Norway is due to the occurrence of organic soil, highest rainfall area, wet climate)

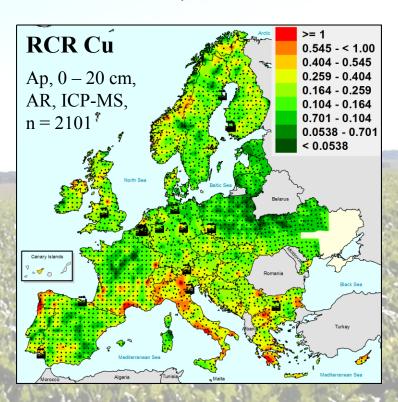




Distribution of predicted no effect concentration (PNEC) and risk characterisation ratio (RCR) for Cu in European agricultural soils

Risk evaluation (RCR = PEC/PNEC)





- > Direct risks for terrestrial organisms (RCR > 1) are only predicted for few isolated sites (1.5 % of all Ap and 1.3 % of all Gr samples).
- > Usually land use is "vineyard" in these locations (application of Cu based fungicides).





Conclusions:

- Low density geochemistry is a viable approach to map the geochemistry of European agricultural soils.
- For the first time a consistent and harmonized dataset reporting element concentrations and soil properties that determine the availability of metals in soils is presented in European scale.
- Natural processes (geology and climate) drive the distribution patterns observed in most maps. For many elements we detect a pronounced break in the concentrations and the background between northern and southern Europe along the maximum extend of the last glaciation.
- Anthropogenic impact is sometimes visible but has serious effects at another, much more local scale. The geochemical maps reflect most of known metal mining districts in Europe.
- The GEMAS data allow a directly comparable country-specific regional risk characterisation based on PEC (Predicted Environmental Concentration) and PNEC (Predicted No Effect Concentration) data for 27 EU countries.







GEMAS - The Project Group





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LATVIJAS VIDES, GEOLOGIJAS UN METEOROLOGIJAS AGENTŪRA

LITHUANIAN

GEOLOGICAL SURVEY





Nationale Bodenbeobachtung Observatoire national des sols Osservatorio nazionale dei suc Swiss Soil Monitoring Network







Service Géologique du Luxembourg



















Appendix

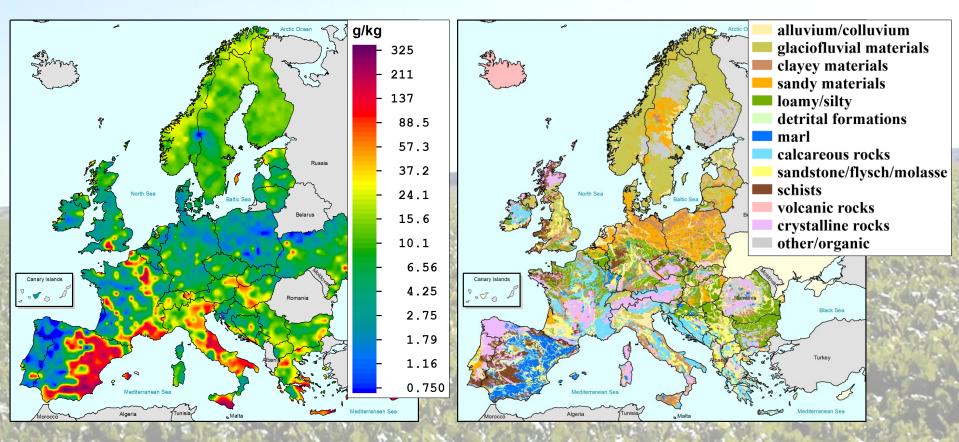




Distribution of total Ca concentration in Ap soils of Europe

Agricultural soils (Ap) (0-20 cm, n=2218, XRF)

Soil parent material (Günther et al., in press)

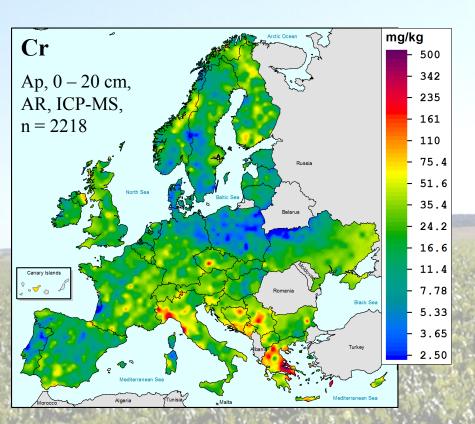


Ca (XRF): areas underlain by calcareous rocks (chalk and limestone)

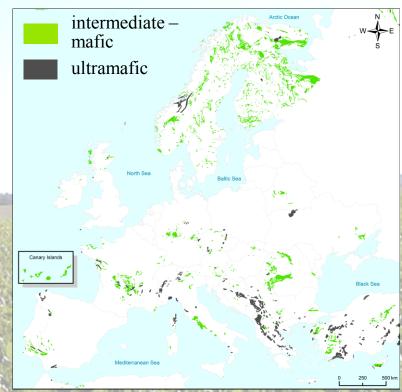




Distribution of chromium (Cr) in agricultural soils (Ap) and the occurrence of intermediate to ultramafic rocks in Europe



Cr: ophiolites (e.g. South-eastern Europe),
greenstone belts, mafic and ultramafic rocks in
south-eastern Europe (e.g. Greece, Cyprus)
→ geological influence

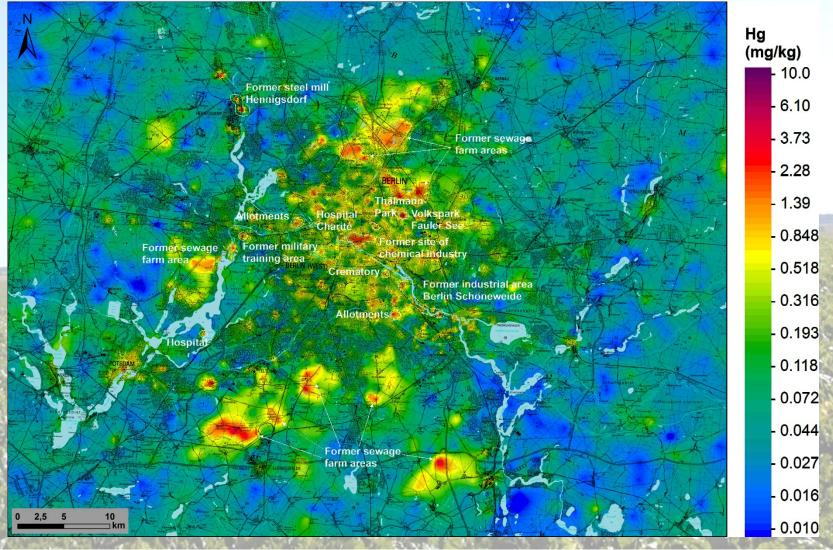


Rock units at the surface (e.g., ophiolite complex) with intermediate to ultramafic igneous rocks an their metamorphic equivalents (F. Jähne)





Distribution of mercury (Hg) in topsoils in the Berlin urban area

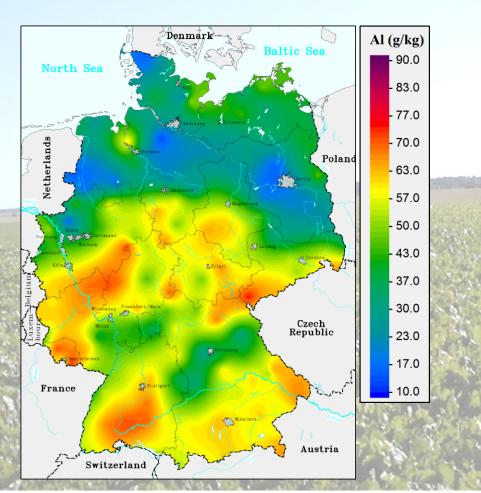


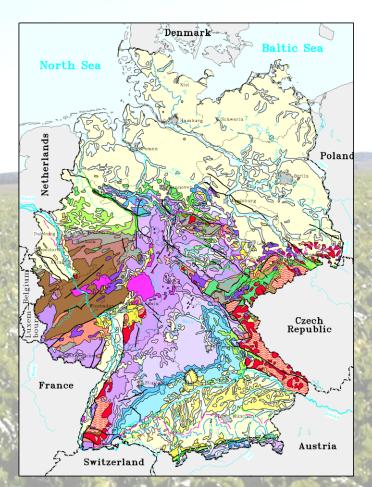




Distribution of Al in Ap soils of Germany

Agricultural soils (Ap) (0 – 20 cm, n = 145, AR, ICP-MS) Geological map









Distribution of Cd (MMI® extraction) in European and German agricultural soils

mg/kg

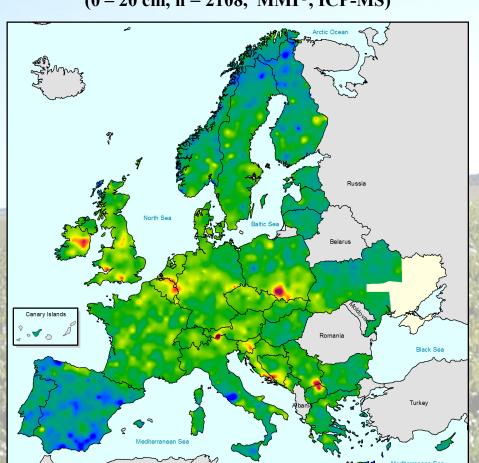
0.800

0.557 0.387 0.270 0.188

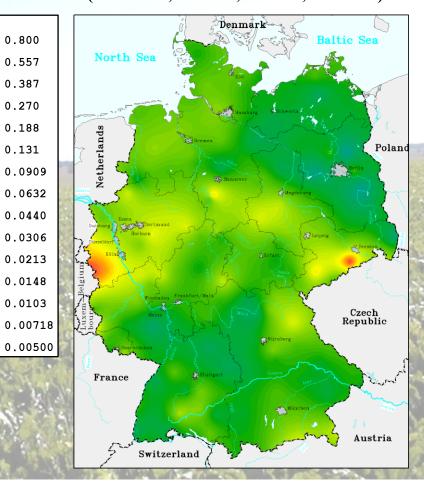
0.131 0.0909

0.0632 0.0440 0.0306 0.0213 0.0148 0.0103

Cd in European agricultural soils $(0-20 \text{ cm}, n = 2108, \text{ MMI}^{\circ}, \text{ICP-MS})$



Cd in German agricultural soils $(0-20 \text{ cm}, n = 143, \text{ MMI}^{\circ}, \text{ICP-MS})$







All GEMAS results will be published in 2013 in the form of a book, accompanied by a CD-ROM including the raw data – the data will thus become public available – just like the data from previous products of EGS.



