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EuroGeoSurveys WORKSHOP

GEochemical Mapping of Agricultural and grazing land Soil in Europe (GEMAS)

http://gemas.geolba.ac.at/

Date: 5 December 2013
Venue: FAO Headquarters in Rome
Organiser: EGS Geochemistry Expert Group
Supported: Eurometaux, FAO, GSP

WORKSHOP AIM

The workshop showed selected case studies demonstrating possible uses of the GEMAS data set. In addition, a twin-like project carried out by the USGS and covering the Conterminous United States was presented, as well as preliminary results from a European Commission soil survey. Examples for the importance of scale and of the selection of the optimal sample density for a given purpose will also be highlighted.

BACKGROUND

Clean, productive agricultural soil is a vital European resource.

- Is European agricultural soil of good quality?
- Is there evidence for large-scale industrial contamination of European agricultural soil (diffuse pollution)?
- Is there evidence of other anthropogenic impacts on European agricultural soil?
- What are the levels of toxic or potentially harmful elements in European agricultural soil?
- Are there element deficiencies in European soil?
- How large is the natural variation of chemical elements in European soil?
- Are there differences between European countries and, if so, what is the explanation?
- Are geology and climate reflected in the spatial distribution of chemical elements in European soil?

These and similar questions will be answered using the results of the GEMAS project.

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GEMAS in Europe

PROGRAMME

1. **GEMAS: Geochemical mapping of agricultural and grazing land soil at the continental scale** - Clemens Reimann and The GEMAS Project Team (*Keynote presentation delivered at the morning plenary session*)

2. (a) **The use of the GEMAS data for compliance with European Chemicals Legislation** - *Ilse Schoeters and Koen Oorts* and (b) **Use of monitoring data for risk assessment of metals in soil** – *Koen Oorts and Ilse Schoeters*

3. **Prediction of metal and metalloid partitioning coefficients (K_d) in soil using mid-infrared diffuse reflectance spectroscopy**
Les J. Janik, Sean Forrester, Jason K. Kirby, Michael J. McLaughlin, José M. Soriano-Disla and Clemens Reimann

4. **Relevance of GEMAS for soil property mapping**
Rainer Baritz, Dietmar Zirlewagen and Vibeke Ernstsen

5. **GEMAS - soil, geology and health implications**
Anna Ladenberger

6. **Field balances of trace elements at the farm scale in Finland and levels of trace elements on the GEMAS maps**
Timo Tarvainen, Tarja Hatakka and Merja Eurola

7. **Natural and anthropogenic signatures in Irish soil: A view from the local to the continental scale**
Ray Scanlon, Katherine Knights, Mairead Glennon and Patrick O'Connor

8. **The geochemical atlas of agricultural and grazing land soil of Italy based on GEMAS samples**
Benedetto De Vivo, Domenico Cicchella, Stefano Albanese, Enrico Dinelli, Lucia Giaccio, Annamaria Lima and Paolo Valera

9. **Soil geochemistry and mineralogy for the Conterminous United States – Results from the North American Soil Geochemical Landscapes project**
Laurel G. Woodruff, David B. Smith and William F. Cannon

10. **Heavy metal concentrations in European soil**
Rannveig Anna Guicharnaud and Luca Montanarella
Note: Not available for downloading

11. **London's soil chemistry: A continental scale anomaly**
Dee Flight, Andreas Scheib and the Geochemical Baselines Team

12. **GEMAS Workshop - Closing remarks**

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GEMAS: Geochemical mapping of agricultural and grazing land soil at the continental scale

Clemens Reimann and the GEMAS Project Team

Geochemical **M**apping of **A**gricultural and grazing land **S**oil (GEMAS) is a cooperative project between the Geochemistry Expert Group of EuroGeoSurveys and Eurometaux. During 2008 and until early 2009, a total of 2108 samples of agricultural (ploughed land, 0-20 cm) and 2023 samples of grazing land (0-10 cm) soil were collected at a density of 1 site/2500 km^2 each from 33 European countries, covering an area of 5,600,000 km^2. All samples were analysed for 52 chemical elements following an aqua regia extraction, 41 elements by XRF (total), and soil properties, like CEC, TOC, pH ($CaCl_2$), following tight external quality control procedures. In addition, the agricultural soil samples were analysed for 57 elements in a mobile metal ion (MMI®) extraction, Pb isotopes and magnetic susceptibility. The GEMAS project thus provides for the first time fully harmonised data for element concentrations, and soil properties known to influence the bioavailability and toxicity of the elements at the continental (European) scale. The provided database is fully in compliance with the requirements of the European REACH Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals). It also provides valuable information for other European pieces of legislation related to metals in soil.

For many elements (*e.g.*, As, Bi, Co, Cu, Li, Mn, Pb), observed concentrations in north-eastern Europe are up to 3 times lower than in south-western Europe. The break in concentration occurs along the southern limit of the last glaciation and is thus directly related to geology. The variable geochemical background from north to south makes it impossible to define one soil background level for any chemical element that is valid for the whole of Europe. However, areas with increased metal concentrations can be clearly identified, and are most often associated with known mineral districts and mining areas. Some major cities (*e.g.*, London, Paris) are marked by local anomalies of elements like Au, Hg and Pb, typically linked to anthropogenic activities. Element concentrations decrease rapidly towards the surrounding natural background with distance to any one anthropogenic source. For several elements (*e.g.*, Hg, P, S, Se), the regional distribution patterns are strongly affected by climatic conditions favouring the development of organic soil. On all geochemical maps, the effect of diffuse contamination remains invisible at the chosen continental scale and sample density. To reliably detect contamination, mapping at a much higher sample density, *i.e.*, at the local scale, is needed. Agricultural and grazing land soil samples show practically the same distribution patterns over Europe and very comparable element concentrations. This demonstrates the robustness of the low sample density geochemical mapping approach.

The use of the GEMAS data for compliance with European chemicals legislation

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For a number of years Europe has legislation in place to ensure chemicals are produced and used safely in Europe. Accurate assessments related to the soil compartment at regional scale were, however, difficult due to the absence of a robust harmonised monitoring database. The GEMAS data filled this important data gap. This presentation will illustrate the value of the GEMAS data for compliance work with Europe's Chemicals Legislation.

Use of monitoring data for risk assessment of metals in soil

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The background concentration of metals in soil typically varies orders of magnitude at a national or continental scale. Similarly, soil properties affecting the fate, behaviour and bioavailability of metals in the terrestrial environment, *e.g.*, pH, clay content, organic matter content, effective cation exchange capacity, vary strongly among soil types. High (bioavailable) metal concentrations may result in toxic effects to terrestrial organisms, while low concentrations of essential elements may entail a risk for deficiency and suboptimal ecosystem functioning. A sound risk assessment on toxicity or deficiency of elements in soil takes into account this spatial variation. Data availability for all these properties, however, differs largely across countries or regions, and where data is lacking, conservative assumptions are often made. Differences in data availability, therefore, preclude accurate risk assessments on a large (*e.g.*, regional or continental) scale and it makes comparison of country or region specific assessments difficult. The GEMAS project addresses this by providing high quality European wide geo-referenced data on metal concentrations and properties influencing metal bioavailability in agricultural and grazing land soil. The GEMAS data provide a strong basis for more robust risk assessments in Europe, taking into account the spatial variability of both exposure (metal concentrations) and bioavailability of metals in soil. The results allow for a uniform approach for assessment of the risks for both toxicity and deficiency. The use of the GEMAS monitoring data for regional and local risk assessments is discussed, based on examples for Cu and Mo, which occur in soil as a cation and an oxyanion, respectively.

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Prediction of metal and metalloid partitioning coefficients (K_d) in soil using mid-infrared diffuse reflectance spectroscopy

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Solid-solution partitioning coefficients (K_d values) are useful indicators of the mobility and bioavailability of metals in soil. Partition coefficients reveal potential exposure pathways of metals once released into the environment. The analytical determination of K_d values is time-consuming and expensive and, hence, development of a more rapid and cost-effective surrogate method is required. Methods using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), coupled with partial least squares regression (PLSR), are well suited for the prediction of K_d values for metals and metalloids. In this study, diffuse reflectance mid-infrared (MIR®) spectra (4000-400/cm), scanned from 470 GEMAS calibration soil samples and reference K_d data, were used to derive PLSR models for the (1) metallic cations: silver (Ag^+), cobalt (Co^{2+}), copper (Cu^{2+}), manganese (Mn^{2+}), nickel (Ni^{2+}), lead (Pb^{2+}), tin (Sn^{4+}), and zinc (Zn^{2+}); (2) anionic metal and metalloid oxyanions: molybdenum (Mo^{6+} as MoO_4^{2-}), antimony (Sb^{5+} oxidised from Sb^{3+} as Sb_2O_3, which hydrolyses to $Sb(OH)_6^-$), selenium (Se^{6+} as SeO_4^{2-}), tellurium (Te^{6+} as TeO_4^{2-}) and vanadium (V^{5+} as VO_3^-); and uncharged boron (B^{3+} as $H_3BO_3^0$). These models were then used to predict K_d values for the remaining GEMAS set of soil samples (n = 4313). Our results showed that MIR-DRIFT, coupled with PLSR and using soil pH as an auxiliary variable, can be used to predict with good accuracy K_d values for the cationic metals (Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} , Pb^{2+} and Zn^{2+}) and the oxyanions (MoO_4^{2-}, $Sb(OH)_6^-$, TeO_4^{2-}). Indicator quality was found for the models developed for the prediction of the K_d values of $H_3BO_3^0$ and VO_3^-. The capability of the technique is further expanded by the possibility of predicting Kd values *in-situ* in the field using DRIFT hand-held spectrometers.

Relevance of GEMAS for soil property mapping

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The GEMAS data set was given to a soil mapping team with the task to test its' use for regional soil property assessments. Total carbon, pH and phosphorus values were upscaled on the basis of regional regression models. This approach provides spatially explicit estimates of important elements at landscape level. The uncertainties of the resulting raster data sets can be quantified, and then can be made available to soil modellers. Not only do such assessments help to understand the quality of the representativeness of the GEMAS inventory, given the variability of soil and landscape in Europe, it also helps to relate dynamic topsoil properties to more stable geochemical, rock-dependent soil properties.

GEMAS – Soil, geology and health implications

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The GEMAS Project resulted in a large coherent data set displaying baseline levels of elements in agricultural and grazing land soil, which has a wide variety of applications. Medical geology is an emerging new discipline providing a link between geoscience and medicine by interpreting natural geological factors in relation to human and animal health and their geographical distribution. Medical geology shows not only problems related to harmful health effects of natural geological materials and processes, but also deals with their beneficial aspects.

Since the GEMAS project demonstrates the importance of geological factors in geochemical patterns in European soil, this data set can be used in improving our understanding of how the geological processes may affect human health in Europe. The main potential health problems are related to deficiency of nutrients in soil and toxic effects of potentially harmful elements. Deficiency in macro- (*e.g.*, K, Fe, Mg, P) and micro-nutrients (*e.g.*, Se, Zn, Cl) can be responsible for a reduction in crop productivity and certain health issues for livestock and humans. On the other hand, bioavailability of crucial elements depends on soil parameters, *e.g.*, pH; namely, low pH in soil (in northern Europe) makes more micronutrients bioavailable, with the exception of Mo, P and Ca. Rocks underlying the soil layer have a major impact on soil composition, and soil parent material can be a main source of toxic metals, for instance, soil developed on black shale (*e.g.*, Oslo region) shows potentially toxic levels of metals, such as As, Cd, U, Zn and Pb. High content of organic matter is another factor amplifying the toxic levels of metals in soil.

Several important topics with health implications can be then addressed using the GEMAS data set, namely, soil properties and element bioavailability, arsenic toxicity, selenium deficiency, potential health effects of liming, uranium in European soil, influence of recent and historical volcanic activity on soil composition and its health consequences.

Field balances of trace elements at the farm scale in Finland and levels of trace elements on the GEMAS geochemical maps

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Field balances of trace elements at the farm level on dairy and crop farms were studied as a part of a three-year (2004-2007) project entitled "*Assessment and reduction of heavy metal input into Finnish agro-ecosystem*". Five crop farms were selected from south-western Finland, typical to arable farming, and five dairy farms from Ostrobothnia, typical to milk production. Concentrations of As, Cd, Hg, Cu, Cr, Ni, Pb, Se, V and Zn were studied from agricultural production resources imported to and products exported from the farms. In addition, topsoil and subsoil samples were analysed.

Balance calculations were made with RAKAS and AROMIS models. The balances of Cd and Hg were slightly positive leading in accumulation of these elements into the topsoil. However, the concentrations of these harmful metals are rather low in Finnish agricultural soil in the European GEMAS data set. In some cases, elevated Hg content was found in organic rich pasture soil.

A major source of selenium on both farm types was the fertilised products. The field balance of Se was highly positive in both farm types. Selenium was enriched sometimes in topsoil in the balance study farms and the earlier Baltic Soil Survey indicated Se enrichment in Finnish agricultural topsoil. According to the GEMAS data, Se concentration is higher in south-eastern Finland compared to general level in agricultural soil of north-eastern Europe.

The Cu and Zn balances were positive on the dairy farms, but on the crop farms they were clearly negative. According to the GEMAS results, Cu concentrations are usually lower in north-eastern Europe compared to southern and western Europe. Thus, the depleting Cu trend in Finnish topsoil in crop farms should be monitored. The concentration of Zn in Finnish agricultural soil was closer to the European average compared to the Cu concentrations in the GEMAS data set. In general, input and outputs of As, Cr, Ni, Pb and V were rather well balanced.

Natural and anthropogenic signatures in Irish soil: A view from the local to the continental scale

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Geochemical surveys have been conducted on Irish soil at a variety of scales over the last decade or so. Surveys of low density at a national scale (one sample per 500 km^2), regional TELLUS surveys of an intermediate scale (one sample per 2-4 km^2) and urban surveys of high density (4 samples per 1 km^2) have been carried out across various parts of the country. Interpretation of these survey data has focused on identifying both the natural (geogenic) and the additional anthropogenic signatures that control the spatial distribution of elements.

It is clear from GEMAS data that geological domains and climatic processes can be readily identified from an extremely low sample density survey at a continental scale. However, anthropogenic inputs from polluting or contaminating industries, from diffuse pollution or agricultural practices are largely undetected at this scale. Higher sample density surveys are required to understand these better and to constrain the spatial patterns and extent of such sources.

In an extensively glaciated terrain, such as Ireland, the soil composition is primarily controlled by the soil parent material and the local bedrock geology; however, human influence - either through diffuse pollution or agricultural practice - may bear an additional signature that can be revealed through the careful examination of the data at differing scales.

The distribution of Zn, Pb, Cd, As, Hg and other elements shows contributions from both natural and anthropogenic inputs, which are revealed differently by surveys at different scales. These are controlled by various combinations of zones of mineralisation, legacy mine sites, urban contamination or agricultural land uses.

The effects of urbanisation are detectable across the range of data sets, and the impact of diffuse pollution in a generally non-industrialised landscape can still be detected at the regional to national scale. The use of urban soil data can help in understanding and quantifying the fine line between what is natural and what is anthropogenic.

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The geochemical atlas of agricultural and grazing land soil of Italy based on GEMAS samples

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The Geochemical Atlas of Italian agricultural and grazing land soil, as part of the GEMAS project, characterises soil of rural areas. Soil samples were collected at an average sampling density of 1 site per 2500 km^2. Two different sample types were collected: (a) 121 samples of agricultural soil on regularly ploughed land to a depth of 20 cm and (b) 121 samples of grazing land soil (land under permanent grass cover) to a depth of 10 cm. All soil samples were air dried, sieved to <2 mm, homogenised and finally split into 10 sub-samples. Both sample types (Ap and Gr) were analysed at the BGR in Berlin for a suite of 41 elements by WD-XRFS. The same samples were also analysed after aqua regia and MMI® extractions by a combination of ICP-AES and ICP-MS for 53 elements. In addition, other parameters were determined: pH, TOC, total carbon and total sulphur, LOI, eCEC, Sr-isotopes, Pb-isotopes, MIR®-spectra. Georeferenced data of the Italian territory were processed by GIS to produce geochemical maps of all determined elements and parameters for both agricultural and grazing land soil. Specifically, for each determinand and sampling medium a map showing interpolated data and graduated dots was produced; univariate statistics and graphs are also displayed on each map. In addition, the Italian GEMAS Atlas includes maps for regional variability of factor scores of elemental associations resulting from R-mode factor analysis, background maps and 15 land use maps for some selected elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V, Zn), following the environmental intervention criteria established by Italian Law (D.L. 152/06).

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Soil geochemistry and mineralogy for the Conterminous United States – Results from the North American Soil Geochemical Landscapes project

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The North American Soil Geochemical Landscapes Project (NASGLP) was designed to develop a continental-scale soil geochemical database for all of North America. As part of the NASGLP, the U.S. Geological Survey collected soil samples at randomly selected sites throughout the conterminous United States (4857 sites, sampling density of ≈1 site per 1,600 km^2). In Canada, soil samples were collected across the Maritime Provinces by the Geological Survey of Canada and provincial surveys (177 sites, sampling density of ≈1 site per 400 km^2), after which the country-wide effort was suspended. Sampling in Mexico by the Servico Geológico Mexicano (1283 planned sites, sampling density of ≈1 site per 1,600 km^2) is nearing completion. All three countries recognised the need to collect a suite of three 'core' samples using consistent sampling protocols: (1) a sample from a depth of 0 to 5 cm, regardless of soil horizon, (2) a composite of the soil A-horizon (uppermost mineral soil), and (3) a sample of deeper subsoil typically from 80 to 100 cm depth (soil B- or C-horizon). In all countries, the <2 mm fraction of each sample was analysed for major and trace elements. In the United States, mineralogical components were quantified for the soil A- and C-horizons.

For the United States data set, spatial differences in geochemistry and mineralogy at continental and regional scales can be tied to distinctive soil parent materials modified by climate-related processes, such as weathering and glaciation. Element distributions, among the three soil samples from each site, reveal human influences superimposed on natural soil background concentrations. This new data set represents a major step forward from prior national-scale soil geochemistry data and, along with a soil archive of all soil samples, provides a robust soil data framework for the United States now and into the future.

All geochemical and mineralogical data with accompanying land use/land type information will be publically released in 2013 as downloadable files. This new data set for the conterminous U.S. represents a major step forward from prior national-scale soil geochemistry data and, along with the soil archive, provides a robust soil data framework for the U.S. now and into the future.

Heavy metal concentrations in European soil

Rannveig Anna Guicharnaud, Luca Montanarella

Note: Presentation not available for downloading

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In 2009, the European Commission launched a soil survey to sample and analyse the main properties of topsoil in 23 Member States of the European Union (EU). This topsoil survey represents the first operational soil survey of this size and ambition at EU level to build a consistent spatial database of topsoil properties across the EU Member States for policy making purposes, based on standard sampling and analytical procedures. Approximately 22,000 points were selected out of a 2 x 2 km grid for the collection of samples. A standardised sampling procedure was used to collect soil, and samples were dispatched to one single central laboratory for physical and chemical analyses. All samples have been analysed for the percentage of coarse fragments, particle size distribution (% clay, silt and sand content), pH (in $CaCl_2$ and H_2O) and cation exchange capacity (cmol(+)/kg), and the levels of organic carbon (g/kg), carbonate (g/kg), phosphorous (mg/kg), total nitrogen (g/kg), and extractable potassium (mg/kg). In 2011, heavy metals analyses were added to the survey and include As, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, Cd and Sb (mg/kg). Preliminary results for the distribution of topsoil properties, including heavy metal concentrations in European agricultural soil, will be presented.

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London's soil chemistry: A continental scale anomaly

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The spatial variation of soil chemistry in maps generated by the GEMAS project shows features of element distribution that are significant at the European continental scale. Natural geological factors are clearly the most important control on the elemental distributions, but environmental changes caused by human activities can also be identified and measured. In the UK and Ireland region, a series of metal anomalies (Pb, Sn, Sb and precious metals) are identified in the low density GEMAS survey in agricultural soil in south-east England, around London. Much higher resolution systematic soil geochemical mapping of London, undertaken by BGS, has confirmed the GEMAS anomalies, and provided unique knowledge of anthropogenic changes to the soil chemistry of the UK's biggest city in which 10 million people live.

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