

## Evaluation and management of arsenic contamination in agricultural soil and water -AgriAs

Arsenic concentrations in agricultural soils and					
waters at the European level					
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## ABSTRACT

**Tarvainen, T., Hatakka, T. 2017.** Arsenic concentrations in agricultural soils and waters at the European level. Evaluation and management of arsenic contamination in agricultural soil and water – AgriAs Deliverables/WP1. 35 pages, 7 figures, 6 tables.

AgriAs Task 1.1 Assessment of data availability on As concentrations in water, soil and crops in Europe has summarized European-wide databases and publications on As concentrations in soil and water. This was followed by a literature review and a questionnaire on national-level data sources concerning As concentrations in agricultural soil and water. The general findings of As concentrations in crops were summarized from the literature. Following the assessment of data availability, a list of major data gaps has been reported. This project report provides a summary of European-wide databases and publications on As concentrations in agricultural soils and related water bodies, the general findings of As concentrations in crops and a list of data gaps.

The literature review and the AgriAs questionnaire revealed that there is a large amount of nationwide or large-scale data on arsenic concentrations in soil, surface water and/or groundwater from many of the Water JPI member countries. However, none of the countries has published regional maps of arsenic concentrations in crops. According to the literature review and the questionnaire, no national-scale data on As concentrations in groundwater, stream water, sediment or topsoil are available from Belgium, Denmark, Estonia, Greece, Latvia, Moldova or Romania. There are no data from European-wide mapping programmes for two countries: Moldova and Turkey.

There is no up-to-date map of arsenic concentrations in European groundwaters related to agricultural sites. The FOREGS geochemical mapping programme measured arsenic concentrations from small headwater streams in 26 European countries, but only a few of the catchment areas were dominated by agricultural land use.

There are quite extensive European-wide datasets on As concentrations in agricultural soil, but more detailed regional mapping at the national level is needed, especially in those areas where anomalously high As concentrations in topsoil have been discovered. According to the AgriAs questionnaire and literature study, European-wide data, as well as the nationwide data, on As concentrations in crops are almost completely lacking.











## Contents

ABSTRACT	2
1. Introduction	4
2. European-wide data availability from the literature	4
2.1 FOREGS - Geochemical Atlas of Europe	4
2.2 Baltic Soil Survey	10
2.3 GEMAS – Geochemistry of European agricultural and pasture soils	11
2.4 LUCAS – Topsoil survey	13
2.5 Summary of European-wide data availability from the literature	13
3. Questionnaire	14
3.1 Results of the questionnaire	15
3.2 General findings	15
3.3 Responses according to country	16
3.4 Conclusions of the questionnaire	20
4. Literature review: data availability on the national level	20
4.1 Data availability according to country	20
4.2 Discussion: Data on National level	23
5. Arsenic in crops and water	23
5.1 Interactions between arsenic in soil, water and crops	23
5.2 Arsenic concentrations in food and water	25
6. Data gaps	26
6.1 Data gaps – Discussion	29
Acknowledgements	30
References	31
APPENDIX I Questionnaire concerning national or large-scale regional data on arsenic	
concentrations in soil, water and crops	



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## 1. Introduction

AgriAs Task 1.1 Assessment of data availability on As concentrations in water, soil and crops in Europe has summarized European-wide databases and publications on As concentrations in soil and water. This was followed by a literature review and a questionnaire on national-level data sources of As concentrations in agricultural soil and water. The general findings concerning As concentrations in crops were summarized from the literature. Following the assessment of data availability, a list of major data gaps has been reported. This project report provides a summary of European-wide databases and publications on As concentrations in agricultural soils and related water bodies, the general findings of As concentrations in crops and a list of data gaps.

## 2. European-wide data availability from the literature

There are numerous arsenic-related publications and reports, but many of them focus on arsenic problems in South-East Asia or are limited to groundwater or contaminated soil. The AgriAs project has focused on European data on agricultural soil and related surface water or groundwater.

## 2.1 FOREGS - Geochemical Atlas of Europe

The main aim of the FOREGS Geochemical Baseline Mapping Programme was to provide high-quality, multi-purpose environmental geochemical baseline data for Europe. The mapping programme was carried out by European geological surveys: first by the Forum of European Geological Surveys (FOREGS) and later by EuroGeoSurveys (http://www.eurogeosurveys.org/). The geochemical data were based on the analysis of samples of stream water, stream sediment, floodplain sediment (or alluvial soil), residual soil and humus collected from 26 European countries. The high quality and consistency of the data were ensured by using standardised sampling methods (Salminen et al. 1998), and by applying rigorous, harmonised quality assurance measures during chemical analysis and subsequent data handling stages (Salminen et al. 2005).

The most interesting sample media for the AgriAs project are stream water and soil. According to Salminen and others (2005), stream waters (Fig. 1) reflect the interplay between the geosphere/hydrosphere and pollution. At the same time, surface waters can be a major source of drinking water. Many surveys have conducted local studies, so the FOREGS data can be used to link results across Europe.

The element concentrations of soil samples reflect variations in the geogenic composition of the uppermost layers of the Earth's crust. Thus, it was important to avoid soil sampling at locations with visible or known contamination. Priority in site selection was given to (Salminen et al. 2005):

- 1. forested and unused lands;
- 2. greenland and pastures; and



**3**. non-cultivated parts of agricultural land (in very special cases, where residual soil could not be found).

The comparison of topsoil and subsoil data provides information on enrichment or depletion processes between the layers. One such process is anthropogenic contamination of the top layer. The <2 mm fraction was analysed according to environmental standards.

Because the soil sampling was focused on residual soils with forest land or unused land, only a small part of the FOREGS soil data represents agricultural soil. Only 151 out of 843 soil sampling sites were classified as agricultural soil in land-use characterization. The total concentration of arsenic in topsoil (0–25 cm) and in subsoil (ca. 50–75 cm) was available from all 151 samples (Fig. 2). The arsenic concentrations of adjacent small headwater streams in surface water (Fig. 3) and in stream sediment (Fig. 4) were available from almost all of these 151 sites.













Fig. 1. Arsenic in European stream water. Number of samples = 807. Detection limit = 0.01  $\mu$ g/l. Source: FOREGS Geochemical Baseline Mapping Programme (Salminen et al. 2005).



Fig. 2. Arsenic in European agricultural topsoil. Total dissolution of the <2 mm size fraction. Number of samples = 151. Detection limit = 0.2 mg/kg. Source: FOREGS Geochemical Baseline Mapping Programme (Salminen et al. 2005).





Fig. 3. Arsenic in European stream water in catchments with agricultural soil sampling sites. Number of samples = 143. Detection limit = 0.2 mg/kg. Source: FOREGS Geochemical Baseline Mapping Programme (Salminen et al. 2005).





Fig. 4. Arsenic in European stream sediment in catchments with agricultural soil sampling sites. Number of samples = 150. Aqua regia extraction. Detection limit = 5 mg/kg. Source: FOREGS Geochemical Baseline Mapping Programme (Salminen et al. 2005).

The highest arsenic concentrations in agricultural topsoils in the FOREGS dataset were measured from samples collected in France, Italy and Spain. A high arsenic concentration in agricultural soil was not always reflected in the arsenic concentration of stream water from the same catchment. Table 1 shows that the As concentration in stream water was not correlated with that in topsoil at the agricultural sampling sites of the FOREGS programme. However, arsenic in stream sediment was positively correlated with topsoil As concentrations. Either arsenic in topsoil and stream sediments has the same (geogenic) source or arsenic has been transported in mineral particles from agricultural topsoil into water bodies.



Table 1. Spearman's rank correlation coefficients between arsenic concentrations in agricultural topsoil, stream water and stream sediment in the agricultural soil sampling sites of the FOREGS dataset (Salminen et al. 2005).

	As (topsoil)	As (stream water)	As (stream sediment)
As (topsoil)	1.000	0.000	0.457**
As (stream water)	0.000	1.000	0.169*
As (stream sediment)	0.457**	0.169*	1.000

\* = Correlation is significant at the 0.05 level (2-tailed);

\*\* = Correlation is significant at the 0.01 level (2-tailed).

## 2.2 Baltic Soil Survey

During 1996–1997, agricultural soils from ten northern European countries (Western Belarus, Estonia, Finland, Northern Germany, Latvia, Lithuania, Norway, Poland, Western Russia and Sweden) were collected at 748 sites from the Ap (0–25 cm) and B/C horizon (50–75 cm) (Reimann et al. 2003). The sample sites were evenly spread over an area of 1 800 000 km<sup>2</sup>, at an average sample density of 1 site / 2500 km<sup>2</sup>. The <2 mm fraction (Poland: <1 mm) of all 1500 samples was analysed for up to 62 chemical elements following ammonium acetate, aqua regia and HF extraction, and for total element concentrations by XRF. Electrical conductivity, pH (water extraction) and loss on ignition (LOI, 1030 °C) were determined as additional parameters. For each of the employed methods, all analyses were carried out in a single laboratory.

Unlike the FOREGS mapping programme, the Baltic Soil Survey sampling only targeted agricultural soils. Figure 5 presents the arsenic concentrations in topsoil and in subsoil. The highest concentrations were observed in Fennoscandia and in South Poland. The anomaly patterns in topsoil and subsoil are almost identical, and most of the arsenic in agricultural soil in northern Europe is therefore probably geogenic. Arsenic concentrations tend to be higher in subsoil.





Fig. 5. Arsenic concentrations in agricultural topsoil (0–25 cm) and bottom soil (50–75 cm). Source: Baltic Soil Survey (Reimann et al. 2003).

## 2.3 GEMAS – Geochemistry of European agricultural and pasture soils

The most promising European-wide data source for arsenic concentrations in agricultural soils is the GEMAS dataset. Reimann and others (2015) describe the GEMAS project as follows: during 2008 and early 2009, a total of 2108 soil samples from agricultural (ploughed land, 0–20 cm) and 2023 soil samples from grazing land (0–10 cm) were collected at a density of 1 site/2500 km<sup>2</sup> each from 33 European countries, covering an area of 5 600 000 km<sup>2</sup>. All samples were analysed for 52 chemical elements after aqua regia extraction, for 41 elements by XRF (total) and for soil properties such as CEC, TOC and pH (CaCl<sub>2</sub>) following tight external quality control procedures. In addition, the agricultural soil samples were analysed for 57 elements in a mobile metal ion (MMI®) extraction, as well as for Pb isotopes and magnetic susceptibility. The GEMAS project thus for the first time provided fully harmonised data on 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).

The concentrations of many elements (e.g., As, Bi, Co, Cu, Li, Mn, Pb) in the soils of northeastern Europe are up to three times lower than in the south-west of Europe. The transition in the concentrations occurs along the southern limit of the last glaciation and is thus directly related to geology. Figure 6 presents the distribution of arsenic in agricultural topsoil. According to Tarvainen et al. (2013), the median As concentration in the agricultural soils of southern Europe was found to be more than 3-fold higher than in those of northern Europe (median values of aqua regia extractable concentrations: 2.5 mg/kg vs. 8.0 mg/kg; median values of total arsenic concentrations: 3 mg/kg vs. 10 mg/kg). Most of the As anomalies on



the maps can be directly linked to geology (ore occurrences, As-rich rock types). However, some features have an anthropogenic origin (Tarvainen et al. 2015).

Tarvainen et al. (2015) described some European-scale arsenic anomalies. In southern and central Europe, many of the arsenic anomalies coincide with known mineral belts, such as the Rhenish Massif, Harz Mountains and Erzgebirge ore districts (Ore Mountains) in Germany or many vein-type As mineralisations in France and the ore deposits in the Iberian Pyrite Belt, Spain. Because most of the known deposits have been mined, local industrial sources often developed in the same areas, and some anthropogenic anomalies can therefore coincide with the geological ones. More detailed geochemical mapping can reveal the difference between geogenic and anthropogenic anomalies. For example, the Geochemical Atlas of Saxony (Rank et al. 1999) covers the Erzgebirge (Ore Mountains) area at a density of 1 sample/16 km<sup>2</sup> and demonstrates that although most of the anomalies can be traced back to known ore bodies, high As concentrations have been spread over a much larger area via anthropogenic activities (mining, smelting). Some anomalies in European agricultural soils may be linked to As-based herbicides having been used in ploughed fields.



Fig. 6. Arsenic concentrations in European agricultural soils (0–20 cm). Source: GEMAS data (Reimann et al. 2015).









## 2.4 LUCAS – Topsoil survey

The LUCAS Topsoil Survey, with its 1 site/200 km<sup>2</sup> sampling, represents the first effort to build a consistent spatial database of soil properties for environmental assessments ranging from the regional to the continental scale on all major land-use types across Europe (http://esdac.jrc.ec.europa.eu/content/lucas-2009-topsoil-data). According to Toth et al. (2015a and b), topsoil geochemistry presents an adequate information base to assess the heavy metal load to the environment and its potential to enter the food chain. Arsenic is one of the potentially harmful elements that has been analysed from topsoil samples in the LUCAS survey. Similarly to the FOREGS and GEMAS programmes, standard sampling and analytical procedures were used in the LUCAS survey and all soil samples were analysed in a single laboratory.

The LUCAS Topsoil Survey revealed similar anomalies to the GEMAS project. The majority of As anomalies on the GEMAS and LUCAS maps coincide with known mineral belts or ore deposits, where As is a frequent by-product. Some anomalies shown on the map can also be due to anthropogenic sources. For example, elevated arsenic concentrations in soil have been found in the Erzgebirge old mining region in Germany. LUCAS demonstrated that As is one of the major threats to the topsoil in Southern Saxony (Toth et al. 2015a).

## 2.5 Summary of European-wide data availability from the literature

The AgriAs project has concentrated on European publications, reports and data related to arsenic. Reimann et al. (2009) have provided a good summary of the European-wide availability of data on As concentrations in soil and water. Table 2 presents the median values of As concentrations in media from those studies that are most the relevant to the AgriAs project.

Reimann et al. (2009) also list several national data sources. Data on arsenic concentrations in soil are available at least from Austria, the Czech Republic, Finland, Germany, Lithuania, Poland, Slovakia and parts of Estonia, Italy, Norway and the UK. Surface water data were available from Finland, Germany and Romania, and groundwater data from Germany, Norway and Slovakia. More up-to-date information on national and regional data sources were identified from the AgriAs questionnaire.









Table 2. Median values of arsenic concentrations in soil (mg/kg) and in water ( $\mu$ g/l) in selected data sources reported by Reimann et al. (2009). FOREGS = FOREGS Geochemical Baseline Mapping Programme (Salminen et al. 2005), BSS = Baltic Soil Survey (Reimann et al. 2003).

Media	Data	Analytical info	As	Reference
	source			
European Union, topsoil	FOREGS	<2 mm, total	7	Salminen et al. 2005
(0–25 cm)		(XRF) (N = 840)		
European Union, topsoil	FOREGS	<2 mm, total (AR)	6	Salminen et al. 2005
(0–25 cm)		(N = 784)		
Northern Europe, topsoil	FOREGS	<2 mm, total	2.3	Salminen et al. 2005
(0–25 cm)		(XRF) (N = 840)		
Southern Europe, topsoil	FOREGS	<2 mm, total	10.5	Salminen et al. 2005
(0–25 cm)		(XRF) (N = 840)		
Northern Europe, agric.	BSS	<2 mm, aqua regia	1.9	Reimann et al. 2003
soil 0–25 cm		(N = 743)		
Northern Europe, agric.	BSS	<2 mm, aqua regia	2	Reimann et al. 2003
soil 50–75 cm		(N = 746)		
Northern Europe, agric.	BSS	<2 mm, HF	2.3	Reimann et al. 2003
soil 0–25 cm		(N = 747)		
Northern Europe, agric.	BSS	<2 mm, HF	2.3	Reimann et al. 2003
soil 50–75 cm		(N = 747)		
Northern Europe, agric.	BSS	<2 mm, XRF	4	Reimann et al. 2003
soil 0–25 cm		(N = 747)		
Northern Europe, agric.	BSS	<2 mm, XRF	4	Reimann et al. 2003
soil 50–75 cm		(N = 747)		
Stream water, European	FOREGS	Filtered <0.45 µm	0.63	Salminen et al. 2005
Union		(N = 807)		
Stream water, N Europe	FOREGS	Filtered <0.45 µm	0.27	Salminen et al. 2005
Stream water, S Europe	FOREGS	Filtered <0.45 µm	0.68	Salminen et al. 2005

The newest data sets of the EuroGeoSurveys GEMAS mapping project and JRC LUCAS data were not included in the literature review by Reimann et al. (2009).

## 3. Questionnaire

A web-based AgriAs questionnaire on national and large-scale regional data sources on arsenic in soil, surface water, groundwater and crops in Europe (Appendix I) was sent in May 2017 to 116 organizations from 23 countries: Austria, Belgium, the Czech Republic, Croatia, Denmark, Finland, France, Germany, Greece, Hungary,

Ireland, Italy, the Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Turkey, Ukraine and the United Kingdom. The selected organizations represented environmental authorities and research organizations working on water quality, (agricultural) soil and environmental issues.



## 3.1 Results of the questionnaire

This chapter summarizes the results of the web-based AgriAs questionnaire on national and large-scale regional data sources on arsenic in soil, surface water, groundwater and crops in Europe. The number of respondents was 13 (ca. 10%). Responses came from Finland, France, Germany, Spain, Sweden and Turkey

After entering the name and country of their organization, the respondents were asked if any national or large-scale regional data are available on arsenic in soil, surface water, groundwater or crops. Altogether, 58% of the respondents stated that data exist on arsenic concentrations in soil and 33% reported that there are data on arsenic in surface water and groundwater, but none of the respondents had knowledge of large-scale data on arsenic concentrations in crops.

The answers to the questions related to soil data indicated that all the datasets were fully or at least partly publicly available. The respondents provided links to eight web pages and/or reports.

The answers to the detailed questions on surface water data showed that all the datasets were fully or at least partly publicly available. The respondents provided two links to three web pages and two contact addresses for further questions.

According to the responses to the detailed questions related to groundwater, all the datasets are fully or at least partly publicly available. The respondents provided two links to three web pages.

The results of this questionnaire did not reveal any data available on arsenic concentrations in crops at the regional level. In the free comments section, three respondents provided information on data availability.

## 3.2 General findings

Ten per cent of the stakeholders to whom the questionnaire was sent provided responses. However, even with the small number of respondents, this questionnaire revealed that regional-scale data are available on arsenic concentrations in soil and surface water. These data can provide a detailed insight into the European-wide anomalies found in the FOREGS (Salminen and others 2005), GEMAS (Reimann and others 2015; Tarvainen and others 2015) and LUCAS surveys (Tóth and others 2015a; 2015b). In addition, regional or national data are available on arsenic concentrations in groundwater, which have been lacking from the European-wide geochemical mapping programmes. Unfortunately, no publicly available national or regional datasets were reported on arsenic concentrations in crops.



## 3.3 Responses according to country

#### <u>Finland</u>

The Geological Survey of Finland (GTK) holds data on arsenic in the most common soil parent material in Finland, glacial till. The whole country has been covered by geochemical mapping at the reconnaissance scale (1 sample/300 km<sup>2</sup>; Koljonen 1992). More detailed data and also data from other soil parent materials (sand, clay) are available from selected geochemical province areas. Unfortunately, only a few sampling sites represent agricultural soil.

In addition to soil geochemistry, GTK has arsenic data from small headwater streams (Lahermo et al. 1996) and groundwater (Lahermo et al. 2002). Stream water data are publicly available, and groundwater data can be used as regionally aggregated data. Spatial data are available from the Hakku server (<u>https://hakku.gtk.fi/en</u>).

The Natural Resources Institute Finland (Luke) has data on arsenic concentrations in agricultural soil (Mäkelä-Kurtto et al. 2007a). Field balances of arsenic at the farm level on crop and dairy farms in Finland have been investigated in the RAKAS project (Mäkelä-Kurtto et al. 2007b).

#### <u>France</u>

The French National Institute for Agricultural Research (INRA) provided a link to soil arsenic data in France. Soil data are available on As concentrations at the national scale (monitoring network, 2171 plots in metropolitan territory). The web server <a href="http://www.gissol.fr/donnees/webservices">http://www.gissol.fr/donnees/webservices</a> combines soil information on a French user interface. However, arsenic concentration data are not yet available on this web page, and the data still require validation before publication.

#### <u>Germany</u>

Five German States (Länder) provided answers to the questionnaire. In addition, the AgriAs project has detailed information on Saxony from a study site in the Freiberg area. Web-based information systems are available for each federal state providing data on soil and water. However, in some cases, access to data is restricted or only possible after registration or application. Table 3 summarizes the responses from the five states that answered the online questionnaire, as well as the researched states providing a web-based information system.

In the detailed comments, a link was provided to the website of the German Working Group on Soil Protection of the Federal States and the Federal Government represented by the Federal Environmental Ministerium (LABO). This website includes a report on the background organic and inorganic pollution of the soils in Germany (<u>https://www.labodeutschland.de/Veroeffentlichungen-DatenInformationssysteme.html</u>).



Table 3. Arsenic anomalies reported in European-wide surveys and regional-scale data availability from German states according to the AgriAs project online questionnaire in May 2017 and researched websites. FOREGS: Salminen et al. 2005. GEMAS: Reimann et al. 2015.

	Arsenic anomalies reported at the European level			Large-scale regional data available			
States (Länder)	Water (FOREGS)	Soil (FOREGS)	Soil (GEMAS)	Soil	Surface water	Ground water	Crops
Online questionnaire results							
Hessen	No	No	No	Yes	Yes	Yes	No
Schleswig-Holstein	Yes	No	No	Yes	No	Yes	No
Baden-Württemberg	Yes	Yes	Yes	No	No	No	No
MecklenburgVorpommern	No	No	No	Yes	Yes	No	No
Sachsen-Anhalt	No	No	Partly	Yes	No	No	No
Researched websites:							
Sachsen	No	Yes	Yes	Yes	Yes	Yes	Yes
Nordrhein-Westfalen	No	No	No	Yes	Yes	No	No
Bayern	No	No	Yes	Yes	Yes	Yes	No

Arsenic concentrations in soil and surface water in *Hessen* are at the typical level for southern and western Europe in European-wide surveys. Regional data are available for soil, surface water and groundwater. In European-wide interpolated maps, the topsoil arsenic concentration is usually 6–9 mg/kg (aqua regia extraction). The median value from regional studies is 9 mg/kg (aqua regia extraction; Hessisches Landesamt für Umwelt und Geologie 2011).

Only 3–4% of groundwater samples had arsenic concentrations higher than the limit value of 10  $\mu$ g As/l (Hessisches Landesamt für Umwelt und Geologie 2013).

The soil background values for arsenic are available from a web-based map server (Fig. 7) of *Schleswig-Holstein* 

(http://www.umweltdaten.landsh.de/atlas/script/index.php). The mapping area is dominated by low arsenic concentrations (<6.95 mg/kg). In the geochemical maps of European soil, this region also mostly shows As concentrations of 2–6 mg/kg. The highest class in the map server is >14.5 mg/kg (95<sup>th</sup> percentile), and arsenic concentrations tend to be higher in the western part of Schleswig-Holstein. Statistics on arsenic concentrations in different soil types and land-use classes are published in LLUR (2011).





Fig. 7. Screen shot from the map server showing background values for arsenic in soil in Schleswig-Holstein, Germany

(<u>http://www.umweltdaten.landsh.de/atlas/script/index.php</u>). Source: Schleswig-Holstein Ministerium für Energiewende, Landwirtschaft, Umwelt und ländliche Räume.

According to the European-wide geochemical maps, arsenic concentrations in *Baden-Württenberg* are higher than in most other areas of Germany. The questionnaire did not reveal any new regional datasets.

*Mecklenburg-Vorpommern* reported that there are regional data on arsenic in soil and in surface water. Soil data are available via the LABO website (https://www.labodeutschland.de/Veroeffentlichungen-Daten-Informationssysteme.html).

*Sachsen-Anhalt* has reported arsenic concentrations in various types of soil areas. For example, in the upper part of agricultural soils of loess areas, the median arsenic concentration was 11 mg/kg, while in lowland sandy soils, the median was only 3 mg/kg (Landesamt für Geologie und Bergwesen Sachsen-Anhalt 2014).

Besides the responses from the questionnaire, further information from *Sachsen* has been published online for As in water

(https://www.umwelt.sachsen.de/umwelt/wasser/7112.htm for surface water; https://www.umwelt.sachsen.de/umwelt/wasser/6198.htm#article15124 for groundwater). Geochemical maps of As and heavy metals in topsoil as well as in subsoil are available online at https://www.umwelt.sachsen.de/umwelt/boden/23273.htm or in maps (GcBÜK 40). For the area of Freiberg, varietal trials on arsenic accumulation in



different crops have been carried out, and information is thus also available for As in crops. The highest concentrations of As can be found in the area of the ore mountains in the south of Sachsen due to mining activities. The concentration range in topsoil lies between almost 0 mg/kg and 2300 mg/kg (LfUG 2001).

The Federal State of *Nordrhein-Westfalen* provides online maps presenting soil contamination with As and other pollutants (<u>https://www.stobo.nrw.de/?lang=de</u>). Information on As in surface water has also been published (<u>http://luadb.it.nrw.de/LUA/hygon/pegel.php</u>).

For *Bayern*, soil characteristics and *aqua regia* extracts from top- and subsoil are published at <u>http://www.umweltatlas.bayern.de</u>. Information for water is provided by LfU online at <u>https://www.lfu.bayern.de/wasser/grundwasserbeschaffenheit/geogene\_einfluesse/ar</u> <u>sen/index.htm</u>.

#### <u>Spain</u>

The University of Huelva reported that there are no large-scale datasets on arsenic concentrations in soil, crops or water bodies in Andalusia, Spain.

#### <u>Sweden</u>

The Swedish Geotechnical Institute and Swedish University of Agricultural Sciences (SLU) provided information from Sweden. SLU maintains a web server, 'Miljödata MVM', for soil, water and environmental data (http://miljodata.slu.se/mvm). The user can select the sampling medium (surface water), sampling period (e.g. 1991–2017) and parameters (e.g. As concentrations). The query results in an Excel file with the names and coordinates of the sampling sites, time of sampling and As concentrations in the unit  $\mu$ g/l. In the European-wide FOREGS maps, As concentrations in Swedish stream water are generally low (<0.63  $\mu$ g/l), except for the Boliden/Skellefteå ore district in northern Sweden. The soil geochemical maps show elevated As concentrations in the same area, and elevated concentrations of As in groundwater have also been reported (Tarvainen et al. 2015). The median As concentration in all groundwater observations from Swedish monitoring sites during 1991–2017 was 0.38  $\mu$ g/l. Higher than the average concentrations (almost 10  $\mu$ g/l) were measured in groundwater, for example from a station in Örnsköldsvik in northern Sweden. The site belongs to an anomaly already seen on European-wide maps. Single As anomalies have been found at various monitoring sites in different parts of Sweden.

The Geological Survey of Sweden (SGU) maintains a database on soil geochemistry. The main results are available as an atlas book. An open database on soil geochemistry is available via the website <u>http://www.sgu.se/en/products/data/usedata-from-sgu/</u>.

#### <u>Turkey</u>

Selcuk University, Advanced Technology Research and Application Center (Konya region), briefly completed the AgriAs questionnaire and summarized that in Turkey there are national or large-scale data on As in soil and groundwater. The Scientific and Technological Research Council of Turkey has funded some research projects related to arsenic. Their latest reports are publicly available, but the reports are only available in Turkish.



Dr Orhan Gündüz from the Dokuz Eylul University reported that there is no nationwide inventory that reports arsenic levels in the entire country. There are, on the other hand, discrete project reports, scientific papers or some unpublished data from different parts of the country focusing on some specific aspects of arsenic. For

example, Dr Gündüz has published a few reports and papers on arsenic contamination in groundwater and geothermal water of Turkey (<u>http://kisi.deu.edu.tr/orhan.gunduz</u>).

## 3.4 Conclusions of the questionnaire

The results of the AgriAs questionnaire on data availability reveal that large-scale regional data on arsenic concentrations in soil, surface water and groundwater are available from many European countries. However, regional data only seldom clearly combine data from agricultural soil and adjacent water bodies. European-wide anomalies revealed in continental-scale geochemical mapping are also reflected at the regional level, but much more detailed variation can be seen in the regional mapping. The questionnaire did not reveal any new data on the regional distribution of arsenic on crops in Europe.

## 4. Literature review: data availability on the national level

This chapter summarizes the results of the literature review on national-level data sources of As concentrations in agricultural soil and water. The Summon<sup>™</sup> literature search tool and web search engines were used to find additional information on publications, scientific articles and datasets of national geochemical mapping programmes. The following geochemical data were reported from Water JPI member countries and observer countries in Europe.

## 4.1 Data availability according to country

#### <u>Austria</u>

Geochemical mapping of stream sediments has been carried out in Austria, but geochemical mapping of agricultural soils and adjacent surface water or groundwater was not found from the literature review.

#### <u>Belgium</u>

There is no nationwide geochemical atlas.

#### <u>Cyprus</u>

Soil geochemical mapping has been carried out in Cyprus. Sampling depths were 0-25 cm and 50–75 cm, with a density of mostly 1 sample/1 km<sup>2</sup>, and in mountain areas 1 sample from a 1.4 km x 1.4 km grid cell. Both aqua regia extractable and total analysis included arsenic. Soil samples were not limited to agricultural soils (Cohen et al. 2012).











#### <u>Denmark</u>

There is no nationwide geochemical atlas.

#### <u>Estonia</u>

There is no nationwide geochemical atlas.

#### **Finland**

In Finland, geochemical data are available from agricultural soil, stream water, stream sediments and from groundwater. See the results of the questionnaire survey.

#### <u>France</u>

There is no nationwide geochemical atlas, but according to the questionnaire, soil arsenic data will soon be available through a web server. See the results of the questionnaire survey.

There is a nationwide database and web server on groundwater geochemistry, including fully available data on arsenic concentrations. Link: <u>http://www.ades.eaufrance.fr/</u>

#### <u>Germany</u>

Several older geochemical mapping projects have been carried out in Germany since the 1970s, but nationwide data on arsenic concentrations are lacking. Arsenic data from stream water are now available from the Geochemical Atlas of Germany. A geochemical mapping project was carried out during 2002–2006. The sampling density was 1 sample/380 km<sup>2</sup>, and the total number of stream water samples was 944. Altogether, 75 parameters, including As, were determined (Birke et al. 2006 and 2015). Large-scale regional data are available from several states; see the results of the questionnaire survey.

#### <u>Greece</u>

There is no geochemical atlas of agricultural soil or surface water, but the arsenic problem has been discussed in individual scientific articles (e.g. Casentini et al. 2011).

#### <u>Hungary</u>

Low density geochemical mapping based on floodplain sediment samples from two depths was carried out during 1990–1995. The analysis was based on aqua regia extraction and arsenic was one of the analysed elements. A map of the catchment area is publicly available (Ódor et al. 1997).

#### Ireland and Northern Ireland (UK)

The TELLUS Geochemistry programme has been mapping areas in the NW parts of Ireland and Northern Ireland using topsoil, stream water and stream sediments. In the longer term, TELLUS aims to complete surveying the entire island of Ireland. http://www.tellus.ie/

#### <u>Italy</u>

The whole country was first covered by the FOREGS mapping, and national geochemical maps have been published from the FOREGS data (De Vivo et al. 2008). There are also regional geochemical maps, e.g. from Campania and Sardinia.











#### <u>Latvia</u>

There is no nationwide geochemical atlas.

#### <u>Moldova</u>

There is no nationwide geochemical atlas.

#### The Netherlands

A research project has been carried out to assess the quality of agricultural soil in the Netherlands for a total of 42 different combinations of soil type and soil use selected from 13 agricultural regions in the Netherlands. Arsenic was included in the analysis (Lagas & Groot 1996).

#### <u>Norway</u>

The geochemical atlas is based on overbank sediment samples (GEOKJEMISK atlas for Norge. Del 1: Kjemisk sammensettning av flomsedimenter).

#### <u>Poland</u>

In 1990, the Polish Geological Institute initiated geochemical mapping of the country aimed at determining the actual chemical conditions in the Earth's surficial environments (soils, water sediments and surficial water) and sea-floor deposits in the Polish economic sector of the Baltic Sea. The geochemical mapping on different scales covered the entire area of the country and selected more important urban agglomerations and industrial districts. Approximately 15 100 samples of soils, 16 200 samples of freshwater sediments, 14 600 samples of surface water and 467 samples of marine deposits were collected and analysed (Lis et al. 1997). There have also been regional geochemical studies related to the scope of the AgriAs project (e.g. Loska et al. 2003). As was included in the national monitoring of soil quality in 2015 (http://www.gios.gov.pl/chemizm\_gleb/index.php?mod=pomiary; Institute of Soil Science and Plant Cultivation of Poland).

#### Portugal 1997

The continental area of Portugal has been covered by a soil geochemical survey (1 sample/135 km<sup>2</sup>). The sample media were topsoil and the organic humus horizon. The total number of samples was 652, and among other elements, arsenic was analysed (Inácio et al. 2008).

#### <u>Romania</u>

There is no nationwide geochemical atlas.

#### <u>Spain</u>

The geochemical atlas of Spain includes 14 000 sediment and soil sites (Locutura et al. 2012).

#### <u>Sweden</u>

Nationwide geochemical mapping has been published as an atlas book in Sweden (Andersson et al. 2014). See also the results of the questionnaire survey.

#### <u>Turkey</u>

There is no nationwide geochemical atlas. See also the discussion in the questionnaire survey results.



#### United Kingdom

National geochemical mapping referred to as the Geochemical Baseline Survey of the Environment (G-Base) has been carried out (<u>http://www.bgs.ac.uk/gbase/home.html</u>).

## 4.2 Discussion: Data on National level

This literature review and the AgriAs questionnaire revealed that there is a considerable amount of nationwide or large-scale data on arsenic concentrations in soil, surface waters and/or groundwaters from many of the Water JPI member countries. However, none of the countries has published regional maps of arsenic concentrations in crops. Several countries have data on arsenic concentrations in stream sediments or in overbank sediments. Arsenic concentrations in sediments may reflect the concentrations in soil of the river or stream catchment, as seen in the comparison of the FOREGS topsoil and stream sediment results.

Nationwide or large-scale regional mappings have rarely concentrated on agricultural soil alone; they generally cover various land-use classes. Even where national or regional soil data are available for agricultural soil, comparability with the Europeanwide data sets (FOREGS, BSS, GEMAS, LUCAS) should be carefully checked. At least the following methods in sampling and analysis procedures must be checked and taken into account while comparing the results:

- Sampling depth. In the FOREGS programme, topsoil samples were taken from 0–25 cm, while in the GEMAS programme, the sampling depth for agricultural soil was 0–20 cm.
- Size fraction prepared for chemical analysis. Usually, the <2 mm size fraction is used for soil samples.
- Analytical method. In most cases, the reported arsenic concentrations are based on aqua regia extraction.

## 5. Arsenic in crops and water

This chapter will summarize general findings on As concentrations in crops and water. It is based on a literature review. A large amount of data on arsenic in European food products was available from an EFSA report (EFSA 2009).

## 5.1 Interactions between arsenic in soil, water and crops

Arsenic in soil can be derived from both natural and anthropogenic sources. At the European scale, the distribution of arsenic in agricultural topsoil can be mostly explained by geology (Tarvainen et al. 2013). Arsenic anomalies in the old mining areas are probably a combination









of naturally elevated arsenic concentrations in bedrock and soil parent material and additional deposition from local mining and metal processing industry. In general, atmospheric pollution and the application of phosphate fertilizers can be regarded as the main contributors to anthropogenic arsenic deposition in agricultural soils (EFSA 2009). The application of sewage sludge is one potential anthropogenic source of arsenic. In earlier times, arsenic and arsenic-containing compounds were used as wood preservatives, pesticides and feed additives. Certain terrestrial plants can take up arsenic from soil by root uptake and by absorption of deposited arsenic. Certain species such as rice and some ferns may accumulate substantial levels of arsenic (EFSA 2009). Thus, an increased arsenic concentration in soil can increase the arsenic concentrations in food and animal feeds.

Some European-wide mapping programmes such as FOREGS (Salminen et al. 2005), GEMAS (Reimann et al. 2015, Tarvainen et al. 2015) and LUCAS (Toth et al. 2015a, 2015b) provide a general picture of arsenic concentrations in soil. FOREGS mapping also includes information on arsenic concentrations in surface water. However, there is no up-to-date published map of arsenic concentrations in certain crops. The European Food Safety Authority Panel on Contaminants in the Food Chain (CONTAM Panel; EFSA 2009) has collected data on arsenic in food in Europe and assessed the risk to human health related to the presence of arsenic in food. The highest total arsenic levels were measured in the following food commodities: fish and seafood, food products or supplements based on algae, cereals and cereal products, with particularly high concentrations in rice grains and rice-based products, followed by food for special dietary uses, bottled water, coffee and beer, rice grains and rice-based products, fish and vegetables were identified as largely contributing to the daily exposure to inorganic arsenic in the general European population.

Most data reported for food describe the total arsenic concentration. Far fewer data are available on the type of arsenic (i.e. arsenic species). In humans, soluble inorganic arsenic is nearly completely absorbed after ingestion. Food products of terrestrial origin generally contain low concentrations of total and inorganic arsenic, except rice, which can contain a significant amount of inorganic arsenic. The absorption of different organic arsenic compounds is generally greater than 70%. However, arsenobetaine, the major form of arsenic in fish and most seafood, is not metabolized in humans (EFSA 2009). In Norwegian food samples, the inorganic arsenic level has been found to be low in fish, but high in other types of seafood. In fish, the mean middle bound concentration of inorganic arsenic was 1.6  $\mu$ g /kg ww (wet weight), while in crabs and shellfish, the mean middle bound concentration was 27  $\mu$ g /kg ww according to the Norwegian Scientific Committee on Food Safety (VKM 2016).

Almost all the arsenic in drinking water is present as inorganic arsenic. Arsenic concentrations in both surface water and groundwater are usually less than 10  $\mu$ g/l, but elevated As concentrations are found in some areas. Elevated As concentrations are more often observed in groundwater than in surface water (EFSA 2009).

According to WHO, the greatest threat to public health from arsenic originates from contaminated groundwater. Drinking water, crops irrigated with contaminated water and food prepared with contaminated water are the sources of exposure (WHO 2016).









Irrigation with arsenic-bearing groundwater can lead to elevated arsenic concentrations in agricultural soil and impacts on crop and human health. A repeated input of arsenic in irrigation water can lead to a significant increase in soil As concentrations and enhance As transfer into plants (Gillispie et al. 2015). According to the summary paper of Gillispie and others (2015), elevated arsenic concentrations have been observed in rice, maize, wheat and several vegetables due to the application of As-bearing irrigation water. In addition to input from irrigation water to soil and crops, leaching of arsenic from As-containing agricultural soil can lead to adverse effects on sensitive biota in surface waters (Lehtinen et al. 2014).

In addition to drinking water, rice in particular can take up more arsenic than other foods, and due to its high consumption can contribute significantly to arsenic exposure. The United Nations food standards body Codex Alimentarius Commission recommends that the level of inorganic arsenic in polished rice should not exceed 0.2 mg/kg (FAO 2014; CODEX ALIMENTARIUS COMMISSION 2014). The findings of a study in Ecuador seem to indicate that high concentrations of arsenic in the environment (soil or water) or in the rice stem do not necessarily imply accumulation of the element in the grain (Otero et al. 2016). The uptake of As by other plants (maize, ryegrass, rape and sunflower) from arsenic-contaminated soils has been studied in a greenhouse pot experiment in Switzerland (Gulz 2002).

## 5.2 Arsenic concentrations in food and water

EFSA (2009) reported summary information on the results of a call for data on arsenic (DATEX-2008-001222). EFSA received 100 867 results from food testing carried out in 14 Member States and Norway. Altogether, 55% of the data came from Germany, 16% from Slovakia and 10% from the Czech Republic. Far fewer data were available from Austria, Belgium, Denmark, Estonia, Spain, Finland, France, the UK, Hungary, Norway, Poland and Sweden. Old data prior to 2003 and data with incomplete or incorrect descriptions of the food type or unit, or showing insufficient sensitivity of the analytical method were excluded from further analysis. A total of 77 275 sample results were included in the calculation of arsenic concentrations in the relevant food categories.

Quite a large amount of data was available from tap water and from bottled water, followed by the categories "meat and meat products and substitutes", "edible offal and offal products" and "vegetables, nuts and pulses".

Sampling adjustment factors (SAF) calculated from the German Nutrition Survey (Mensink and Beitz., 2004) were applied when aggregating food sub-category averages to category averages in order to fit the information structure of the Concise European Food Consumption database.

Arsenic concentrations were often lower than the analytical detection limit (LOD) or the limit of quantification (LOQ). The method for taking into account values below the LOD or LOQ will affect the calculated mean and sometimes even the median values. The upper bound (UB) is obtained by assigning the value of LOD to values reported as <LOD and LOQ to values reported as <LOQ. The median concentration of arsenic in cereal grains, excluding rice, was 0.0262 mg/kg (UB, N = 2215) and in rice grains 0.110 mg/kg (UB, N = 1122). Bran and germ



showed an even higher median value of 1.63 mg/kg (UB), but the number of samples was only 13. In leafy vegetables, stem vegetables and root vegetables, the median value was only 0.010 mg/kg. The median arsenic concentration for the food category 'Total for Fruits' was 0.010 mg/kg. For tap water and for bottled water, the median As concentration was 0.0010 mg/kg. In the case of natural mineral water only, a maximum level (ML) of 0.010 mg/L of arsenic is specified in the legislation. Only 0.04% of the bottled water samples exceeded this ML. Statistics for all food categories are summarized in EFSA (2009). However, drinking water can be a major contributor of inorganic arsenic in the diet, especially in areas with high natural levels of arsenic in water.

In Sweden, the National Food Agency has studied arsenic concentrations in food. The highest total arsenic concentrations were measured from fish (median value 1193  $\mu$ g/kg), but the amount of inorganic As in fish was small, with a median value of 2.2  $\mu$ g/kg. The median value in both vegetables and potatoes was <1.4  $\mu$ g/kg (Livsmedelsverket 2017).

In Finland, the RAKAS project studied field balances of trace elements at the farm level on crop and dairy farms in 2004. The mean As concentration in oats was 0.031 mg/kg on dairy farms and 0.010 mg/kg on crop farms. For barley, the respective mean concentrations of As were 0.016 mg/kg (dairy farms) and <0.010 mg/kg (crop farms). The mean concentrations of As were always <0.010 mg/kg for spring wheat, winter wheat and rye. For pea, the mean As concentration was 0.019 mg/kg, and that for rapeseed was 0.040 mg/kg. Field balances were estimated for crop farms located in southwestern Finland and for dairy farms located in Ostrobothnia. In southwestern Finland, atmospheric deposition and fertilizer products were equal sources of As. The main source of As in Ostrobothnia was fertilizer products. In all cases, As was mainly flowing out of the farm via erosion. The balance was negative on crop farms and slightly positive on dairy farms (Mäkelä-Kurtto et al. 2007). Arsenic field balances have also been estimated in Sweden (Andersson 1992). In Sweden, deposition was the dominant source of As and leaching was generally the dominant pathway for removal of As.

## 6. Data gaps

Table 4 summarizes the availability of arsenic data in the largest European-wide or large regional geochemical mapping programmes in the Water JPI member countries of Europe. The data gaps are shown as white cells in the table. The colour codes in the table reveal the relative level of arsenic concentrations in the anomalous areas of the member countries (See Table 5 for classification). A red cell indicates that the highest concentrations in a country are high on the European level in stream water, stream sediment or in agricultural topsoil. An orange colour indicates that the highest As concentrations in a country are slightly elevated at the European level, and a green colour indicates that even the maximum concentrations of As in a country are not over the typical European level. The As levels in stream sediment and in topsoil are defined from the FOREGS data set (Salminen et al. 2005). BSS denotes the Baltic Soil Survey project (Reimann et al. 2003). GEMAS data are presented in Tarvainen et al. (2013) and Reimann et al. (2015). For LUCAS data, only two colour codes (orange and green) are applied: orange means that up to 10% of the agricultural soil samples exceed the lower guideline value of 50 mg/kg designated for the assessment of soil contamination in



Finland (Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007)). Green indicates that the highest concentration in a country in the LUCAS project was <50 mg/kg. This classification was used in the Supplementary Material by Tóth et al. (2015b).

Table 4. Arsenic data availability in the JPI member countries in Europe. The data gaps are shown in white. Colours indicate the relative As concentration level in anomaly areas in each country. Red = high, orange = minor anomalies, green = data available but no European-level As anomalies. White = no data available. See Table 5. Topsoil Ap = Agricultural soil.

Country	FOREGS Agricultural Soil Catchments			BSS	GEMAS	LUCAS
	Stream water	Sediment	Topsoil	Topsoil	Topsoil Ap	Agric. topsoil
Austria						
Belgium						
Cyprus						
Denmark						
Estonia						
Finland						
France						
Germany						
Greece						
Hungary						
Ireland						
Italy						
Latvia						
Moldova						
The						
Netherlands						
Norway						
Poland						
Portugal						
Romania						
Spain						
Sweden						
Turkey						
United Kingdom						



Table 5. Colour codes used in Table 4. Finnish LGV = Finnish Lower Guideline Value designated for soil contamination assessment.

FOREGS Agricultural Soil Catchments			BSS	GEMAS	LUCAS
Stream water	Sediment	Topsoil	Topsoil	Topsoil Ap	Agric. Topsoil
Max <3 µg/l	Max <10 mg/kg	Max <10 mg/kg	Max <10 mg/kg	Max <10 mg/kg	<50 mg/kg (Finnish LGV)
Max 3-7 µg/l	Max 10-25 mg/kg	Max 10-25 mg/kg	Max 10-25 mg/kg	Max 10-25 mg/kg	>50 mg/kg (Finnish LGV)
$Max > 7 \mu g/l$	Max >25 mg/kg	Max >25 mg/kg	Max >25 mg/kg	Max >25 mg/kg	

Table 6 summarizes the arsenic data availability in national-scale geochemical mapping programmes in the Water JPI member countries of Europe. According to the literature review and the questionnaire of this study, no national-scale data on As concentrations in groundwater, stream water, sediment or topsoil are available from Belgium, Denmark, Estonia, Greece, Latvia Moldova or Romania.



Table 6. Data availability in national-scale geochemical mapping programmes in the Water JPI member countries of Europe.

Country	National mapping projects				
	Groundwater	Stream	Sediment	Topsoil	Others
		water			
Austria			Х		
Belgium					
Cyprus				Х	
Denmark					
Estonia					
Finland	х	Х	Х	Х	
France	х			(x)	Topsoil As not yet published
Germany		X			Regional data from states
Greece					
Hungary			X		
Ireland		Х	X	Х	Part of Ireland
Italy					Regional maps
Latvia					
Moldova					
The				Х	
Netherlands					
Norway			х		
Poland		Х	Х	Х	
Portugal				Х	
Romania					
Spain			х	Х	
Sweden				Х	
Turkey	Х			Х	Part of Turkey
United Kingdom			Х	Х	

## 6.1 Data gaps – Discussion

Tables 4 and 6 summarize the data availability according to country. No data in the European-wide mapping programmes are available from two countries: Moldova and Turkey. The online questionnaire revealed that the Scientific and Technological Research Council of Turkey could be the best link to the partly public data in Turkey. The Council provides scientific publications, but unfortunately mostly only in Turkish.

According to a literature review, natural water systems can be affected by arsenic contamination deriving from natural terrestrial geothermal systems (Bundschuh et al. 2013) or



from mining activities (Gemici et al. 2008). Recent scientific papers describing surface and groundwater quality in Moldova did not reveal similar arsenic problems.

There is no up-to-date map of arsenic concentrations in European groundwater related to agricultural sites. The FOREGS geochemical mapping programme measured arsenic concentrations from small headwater streams in 26 European countries, but only a few catchment areas were dominated by agricultural land use.

European-wide or large-scale regional databases very seldom combine arsenic concentrations in agricultural topsoil with concentrations in adjacent surface water or groundwater. No correlation was found between arsenic concentrations in agricultural topsoil and in stream water in a subset of the FOREGS programme that only included catchments in agricultural use.

According to WHO, the greatest threat to public health from arsenic originates from contaminated groundwater. Drinking water, crops irrigated with contaminated water and food prepared with contaminated water are the main sources of exposure (WHO 2016). Thus, it is very important to have relevant nationwide data on As concentrations in groundwater. According to this study, national groundwater data are lacking from almost every JPI member country (Table 6).

Food is another notable pathway for As exposure in humans. An increased arsenic concentration in soil can increase the arsenic concentrations in food and animal feeds (EFSA 2009). There are quite extensive European-wide datasets on As concentrations in agricultural soil, but more detailed regional mapping at the national level is needed, especially in those areas where anomalously high As concentrations in topsoil have been discovered. According the AgriAs questionnaire and literature study, European-wide data as well as nationwide data on As concentrations in crops are entirely lacking. It is necessary for risk assessment purposes to have accurate data on As concentrations in, for example, cereals, vegetables, fruits and berries cultivated in soils with high As concentrations.

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### References

Andersson, A. 1992. Trace elements in agricultural soils. Fluxes, balances and background values. Department of Soil Sciences. Swedish University of Agricultural Sciences, Uppsala. ISBN 91-620-4077-4. ISSN 0282-7298. 40 pp.

Andersson, M., Carlsson, M., Ladenberger, A., Morris, G., Sadeghi, M. & Uhlbäck, J. 2014. Geokemisk atlas över Sverige [Kartografiskt material] = Geochemical atlas of Sweden. Uppsala: Sveriges geologiska undersökning (SGU), 208 pp.

Birke, M., Rauch, U., Raschka, H., Wehner, H., Kringel, R., Gäbler, H.-E., Kriete, C., Siewers, U., Kantor, W., 2006. Geochemischer Atlas Bundesrepublik Deutschland -Verteilung anorganischer und organischer Parameter in Oberflächenwässern und Bachsedimenten. Vorabexemplar, 641 pp. (unpublished).

Birke, M., Rauch, U. & Stummeyer, J. 2015. How robust are geochemical patterns? A comparison of low and high sample density geochemical mapping in Germany. Journal of Geochemical Exploration 154, 105-128.

Bundschuh, J., Prakash Maity, J., Nat, B., Baba, A., Gunduz, O., Kulp, T.R., Jean, J.-S., Kar, S., Yang, H.-J., Tseng, Y.-J., Bhattacharya, P. & Chen, C.-Y. 2013. Naturally occurring arsenic in terrestrial geothermal systems of western Anatolia, Turkey: Potential role in contamination of freshwater resources. Journal of Hazardous Materials 262, 951-959.

Casentini, B., Hug, S.J. & Nikolaidis, N.P. 2011. Arsenic accumulation in irrigated agricultural soils in Northern Greece. Science of the Total Environment 409, 4802 – 4810.

CODEX ALIMENTARIUS COMMISSION 2014. Joint FAO/WHO Food Standards Programme CODEX ALIMENTARIUS COMMISSION. Report of the eighth session of the CODEX Committee on contaminants in foods. The Hague, The Netherlands 31 March – 4 April 2014.

Cohen, D.R., Rutherford, N.F., Morisseau, E. & Zissimos, A.M. 2012. Geochemical patterns in the soils of Cyprus. Science of the Total Environment 420, 250-262.

De Vivo, B., Lima, A., Bove, A.M., Albanese, S., Cicchella, D., Sabatini, G., Di Lella, L.A., Protano, G., Riccobono, F., Frizzo, P. & Raccagni, L. 2008. Environmental geochemical maps of Italy from the FOREGS database. Geochemistry: Exploration, Environment, Analysis 8, 267-277.

EFSA 2009. Scientific Option on Arsenic in Food by EFSA Panel on Contaminants in the Food Chain (CONTAM). EFSA Journal 7, (10), 1351.

FAO. 2014. FAO: Maximum levels for Inorganic arsenic in polished rice. Codex Alimentarius Commission - Geneva 14-18 July 2014. http://www.fao.org/news/story/en/item/238558/icode/



Gemici, Ü., Tarcan, G., Helvaci, C. & Somay, M. 2008. High arsenic and boron concentrations in groundwaters related to mining activity in the Bigadiç borate deposits (Western Turkey). Applied Geochemistry 23, (8), 2462-2476.

Gillispie, E.C., Sowers, T.D., Duckworth, O.W. & Polizotto, M.L. 2015. Soil pollution due to irrigation with arsenic-contaminated groundwater: Current state of science. Current Pollution Reports 1, 1 - 12.

Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007), Finland. <u>https://www.finlex.fi/fi/laki/kaannokset/2007/en20070214.pdf</u>. Accessed 9 October 2017.

Gulz, P.A. 2002. Arsenic Uptake of Common Crop Plants from Contaminated Soils and Interaction with Phosphate. Swiss Federal Institute of Technology Zurich. DissETH No. 14879. Permanent Link:

https://doi.org/10.3929/ethz-a-004525606 Hessisches Landesamt für Umwelt und Geologie. 2011. Hintergrundwerte von Spurenstoffen

in hessischen Böden. URL: <u>http://www.hlug.de/start/boden/hintergrundwerte.html</u> (Last visited 25.7.2017)

Hessisches Landesamt für Umwelt und Geologie. 2013. Grundwasserbeschaffenheitsbericht 2012. ISBN 978-3-89026-374-8. 89 pp.

Inácio, M., Pereira, V. & Pinto, M. 2008. The soil geochemical atlas of Portugal: Overview and applications. Journal of Geochemical Exploration 98, 22-33.

Koljonen, T. (Ed.), 1992. Suomen geokemian atlas. Osa 2 : Moreeni = The Geochemical Atlas of Finland. Part 2: Till. Geologian tutkimuskeskus, Espoo, (218 pp. + 9 app. Maps).

Lagas, P. & Groot, M.S.M. (editors) 1996. Bodemkwaliteitskartering van de Nederlandse landbouwgronden. (Soil quality of agricultural land in the Netherlands). RIVM rapport 714801003. 151 pp.

Lahermo, P.; Väänänen, P.; Tarvainen, T.; Salminen, R. 1996. Suomen geokemian atlas. Osa 3: Ympäristögeokemia purovedet ja sedimentit = Geochemical atlas of Finland. Part 3: Environmental geochemistry stream waters and sediments. Espoo: Geologian tutkimuskeskus. 149 p.

Lahermo, P., Tarvainen, T., Hatakka, T., Backman, B., Juntunen, R., Kortelainen, N., Lakomaa, T., Nikkarinen, M., Vesterbacka, P., Väisänen, U. & Suomela, P. 2002. Tuhat kaivoa Suomen kaivovesien fysikaalis kemiallinen laatu 1999. Geologian tutkimuskeskus, Tutkimusraportti 155.- Geological Survey of Finland. Report of Investigation 155.

Landesamt für Geologie und Bergwesen Sachsen-Anhalt 2014. Bodenbericht Sachsen-Anhalt 2014 Grundlagen, parameter und hintergrundwerte. Mitteilungen zu Geologie und Bergwesen von Sachsen-Anhalt, Band 18, 2014. 74 pp.



Lehtinen, H., Härmä, P., Tarvainen, T., Backman, B., Hatakka, T., Ketola, T., Kuula, P., Luoma, S., Pyy, O., Sorvari, J. & Loukola-Ruskeeniemi, K. 2014. Kiviainesten otto arseenialueilla – opas kiviainesten tuottajille, maarakentajille ja viranomaisille. Summary: Exploitation of aggregates in areas with naturally elevated concentrations of arsenic – Guidelines for producers, earthwork contractors, and authorities. Geologian tutkimuskeskus. Opas 59. 71 pp.

LfUG 2001. Sachstandsbericht Die Schwermetallgehalte der Böden des Freiberger Raumes für die Bewertung der Gefährdungspfade Boden  $\Rightarrow$  Mensch, Boden  $\Rightarrow$  Nutzpflanze und Bo-den  $\Rightarrow$  Grundwasser nach Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV).

Lis, J., Pasieczna, A., Strzelecki, R., Wolkowicz, S. & Lewandowski, P. 1997. Geochemical and radioactivity mapping in Poland. Journal of Geochemical Exploration 60, 39 – 53.

Livsmedelsverket. 2017. Swedish Market Basket Survey 2015. Per capita-based analysis of nutrients and toxic compounds in market baskets and assessment of benefit or risk. Livsmedelsverket (National Food Agency) Rapport 26 – 2017.

LLUR. 2011. Hintergrundwerte stofflich gering beeinflusster Böden SchleswigHolsteinsLandesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig-Holstein.

Locutura, J., Bel-Lan, A., Garcia Cortés, A. & Martínez Romero, S. 2012. Geochemical atlas of Spain (Atlas Geoquímico de España) IGME Instituto geológico y minero de España, Madrid.

Loska, K., Wiechula, D., Barska, B., Cebula, E. & Chojnecka, A. 2003. Assessment of arsenic enrichment of cultivated soils in southern Poland. Polish Journal of Environmental Studies 12, 187-192.

Mäkelä-Kurtto, R., Eurola, M. & Laitonen, A. 2007a. Monitoring programme of Finnish arable land. Aqua regia extractable trace elements in cultivated soils in 1998. Agrifood Research Reports 104.

Mäkelä-Kurtto, R., Laitonen, A., Eurola, M., Vuorinen, A., Pasanen, T., Rankanen, R., Suominen, K., Laakso, P., Tarvainen, T., Hatakka, T. & Salopelto, J. 2007b. Field balances of trace elements at the farm level on crop and dairy farms in Finland in 2004. Agrifood Research Reports 111.

Ódor, L., Horváth, I. & Fügedi, U. 1997. Low-density geochemical mapping in Hungary. Journal of Geochemical Exploration 60, 55- 66.

Otero, X.L., Tierra, W., Atiaga, O., Guanoluisa, D., Nunes, L.M., Frreira, T.O. & Ruales, J. 2016. Arsenic in rice agrosystems (water, soil and rice plants) in Guayas and Los Ríos provinces, Ecuador. Science of the Total Environment 573, 778–787.

Reimann, C., Siewers, U., Tarvainen, T., Bityukova, L., Eriksson, J., Gilucis, A.,



Gregorauskiene, V., Lukashev, V., Matinian, N.N. & Pasieczna, A. 2003. Agricultural Soils in Northern Europe: A Geochemical Atlas. Geologisches Jahrbuch, Sonderhefte, Reihe D, Heft SD 5, Schweizerbart'sche Verlagsbuchhandlung, Stuttgart: 279p. www.schweizerbart.de/9783510959068

Reimann, C., Matschullat, J., Birke, M. & Salminen, R. 2009. Arsenic distribution in the environment: The effects of scale. Applied Geochemistry 24, 1147–1167.

Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. & P. O'Connor (eds.) 2015. Chemistry of Europe's Agricultural Soils. Part A: Methodology and Interpretation of the GEMAS Data Set. Geologisches Jahrbuch Reihe B Heft 102. 523 p.

Sächsisches Staatsministerium für Umwelt und Landwirtschaft.Wasser, Wasserwirtschaft. URL: <u>https://www.umwelt.sachsen.de/umwelt/wasser/index.html</u> (Last visited 04.08.2017)

Salminen, R., Tarvainen, T., Demetriades, A., Duris, M., Fordyce, F. M.,
Gregorauskiene, V., Kahelin, H., Kivisilla, J., Klaver, G., Klein, P., Larson, J. O., Lis,
J., Locutura, J., Marsina, K., Mjartanova, H., Mouvet, C., O'Connor, P., Odor, L.,
Ottonello, G., Paukola, T., Plant, J. A., Reimann, C., Schermann, O., Siewers, U., Steenfelt,
A., Van der Sluys, J., Vivo, B. de, & Williams, L., 1998. FOREGS geochemical mapping
field manual. Geological Survey of Finland, Guide 47, 36 pp.

Salminen, R. (Chief-Ed.), Batista, M.J., Bidovec, M. Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005. Geochemical Atlas of Europe. Part 1 – Background Information, Methodology and Maps. Geological Survey of Finland, Espoo, Finland.

Tarvainen, T., Albanese, S., Birke, M., Ponavic, M., Reimann, C. & the GEMAS Project Team. 2013. Arsenic in agricultural and grazing land soils of Europe. Applied Geochemistry 28, 2 - 10

Tarvainen, T; Birke, M.; Reimann, C.; Ponavic, M. & Albanese, S. 2015. Arsenic anomalies in European agricultural and grazing land soil. Pages 81 – 88 in: C. Reimann, M. Birke, A. Demetriades, P. Filzmoser & P. O'Connor (eds.) Chemistry of Europe's Agricultural Soils. Part B: General Background Information and Further Analysis of the GEMAS Data Set. Geologisches Jahrbuch Reihe B Heft 103. 352 p.

Tóth, G. Hermann, T., Szatmári, G. & Pásztor, L. 2015a. Maps of heavy metals in the soils of the European Union and proposed priority areas for detailed assessment. Science of the Total Environment

Tóth, G., Hermann, T., Da Silva, M.R. & Montanarella, L. 2015b. Heavy metals in agricultural soils of the European Union with implications for food safety. Environment International.



VKM. 2016. Dietary exposure to inorganic arsenic in the Norwegian population. Assessment of the Panel on Contaminants of the Norwegian Scientific Committee for Food Safety. Norwegian Scientific Committee for Food Safety (VKM). VKM Report 2016: 11, ISBN: 978-82-8259-201-7, Oslo, Norway. Available online: <u>www.vkm.no</u>

WHO 2016. Arsenic Fact sheet. Updated June 2016. http://www.who.int/mediacentre/factsheets/fs372/en/



**APPENDIX I** 

# Questionnaire concerning national or large-scale regional data on arsenic concentrations in soil, water and crops

I

Background information

- Country (Menu bar: Albania, Andorra, Armenia, Austria, Azerbaijan, Belarus, Belgium, Bulgaria, Bosnia and Herzegovina, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Georgia, Germany, Greece, Hungary, Iceland, Ireland, Italy, Kazakhstan, Kosovo, Latvia, Lichtenstein, Lithuania, Luxemburg, former Yugoslav Republic of Macedonia, Malta, Moldova, Monaco, Montenegro, Netherlands, Norway, Portugal, Poland, Romania, Russia, San Marino, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey, Ukraine, United Kingdom)
- 2. Region \_\_\_\_\_
- 3. Organisation or institute \_\_\_\_\_

#### II

1. Are there any national or large-scale regional data on arsenic concentrations in:

	Yes	No	I don't know
Soil	0	0	0
Surface water	0	0	0
Groundwater	0	0	0
Crops	0	0	0
TO (TT			

#### If 'Yes' :

Would you please specify the data type, e.g. crop type or regional coverage of the data

If all answers are 'No' or 'I don't know': Thank you for your valuable information and participating in the AgriAs project!

#### If at least one of the answers is 'Yes':

2.1 Are the national or large-scale regional data concerning arsenic concentrations in

#### Soil

- publicly available
- o partly publicly available
- o not publicly available











- I don't know about the availability
- 2.2 Are the national or large-scale regional data concerning arsenic concentrations in Surface water
  - Publicly available o partly publicly available o not publicly available
  - I don't know about the availability
- 2.3 Are the national or large-scale regional data concerning arsenic concentrations in Groundwater
  - publicly available o partly publicly available o not publicly available
  - I don't know about the availability
- 2.4 Are the national or large-scale regional data concerning arsenic concentrations in Crops
  - publicly available o partly publicly available o not publicly available o I don't know about the availability
- 3 Where can these data be found?
  - $\circ$  on a website

Would you please include the link

 $\circ$  in a report

Would you please write the reference



o ther method
 Would you please give the contact information for the institute or person

o I don't know

4 Any other information or comments that you would like to pass on to the AgriAs project

Thank you for your valuable information and participating in the AgriAs project!



















