Geochemical baselines in the assessment of soil contamination in Finland

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by

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ACADEMIC DISSERTATION
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Front cover: Sampling for the urban geochemical mapping project in the city centre of Hämeenlinna. Photo: Timo Tarvainen, GTK.
This study provides an overview on the development of the guidelines and legislation related to soil contamination in Finland, with the main focus on geochemical baselines. The use of geochemical baseline surveys in the assessment soil contamination in Finland and in some other countries is briefly discussed and the current practices in Finland are presented. Finally, the geochemical baselines in the assessment of soil contamination in Finland are outlined with suggestions for further applications and recommendations for future research needs.

The growing demand to increase sustainable land management in urban areas has involved various applications of geochemical surveys. Soil contamination was acknowledged as a leading environmental problem in the industrialized countries in the 1980s. The Government of Finland highlighted the importance of studying the level of soil contamination in Finland in 1988. The practices and guidelines for the assessment of soil contamination have been further developed by the environmental authorities and other interest groups, and in 2007, a Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) was issued. According to the Government Decree (214/2007), the assessment of soil contamination shall be based on a site-specific estimate of the risks to human health and the environment. Three categories of soil screening values, the threshold value and the lower and the upper guideline value, are introduced in the Government Decree (214/2007). The threshold value is used as a trigger value, which if exceeded indicates the necessity for further investigations on potential contamination. The geochemical baseline concentration, however, is regarded as the assessment threshold in areas with a baseline concentration higher than the threshold value. The Government Decree (214/2007) refers both to the natural geological background concentrations of elements and the diffuse anthropogenic input with the term “geochemical baseline”. For estimating the regional or local baseline concentration the upper limit of geochemical baseline variation for potentially harmful elements can be used.

Today, geochemical background information is available from national and regional geochemical mapping surveys, as well as from targeted geochemical baseline surveys, from which geochemical baseline mapping of sub-urban and urban areas has had a special focus on environmental applications and land use planning. The geochemical baseline studies provide information on baseline concentrations for remediation projects, land extraction, land use planning and other urban functions. Furthermore, they provide information for mineral exploration, for studies on the baseline status of the environment, as well as for environment impact assessment. The baseline information can also be applied in multidisciplinary studies such as the protection of human health.

The main sample parent material used in the geochemical baseline studies is minerogenic soil. Both composite and single samples are used. Single samples are often used when the data are targeted for use in
calculating statistics for different soil parent materials and land use patterns. The sampling depth in geochemical mapping is traditionally quite variable, but in urban geochemical baseline studies the main focus is on topsoil. In Finland, the guidelines are given for soil contamination analysis and they are also followed in geochemical baseline surveys. For determining the concentrations of inorganic elements, the samples are to be sieved to the <2 mm fraction following aqua regia extraction or strong nitric acid leach. Different gas chromatographic methods are recommended to be used to analyse organic compounds. For risk assessment purposes, as well as for tracing the origin of elevated concentrations, i.e. whether it is anthropogenic or geogenic, weaker extraction methods provide additional information to be applied in data analysis.

The utilization of geochemical baseline information is important when assessing the possible soil contamination and remediation needs. Regional variation due to differences in the geological environment can be high and should be taken into consideration in contamination assessment. Various sampling materials may reveal different geochemical baseline levels. Finnish legislation supports the use of geochemical baseline information, and the Finnish national geochemical baseline database (TAPIR) provides end-users with nationally comparable and scientifically sound geochemical baseline data that enhance the rationality and transparency of decision-making.

Keywords: environmental geology, geochemical surveys, baseline studies, chemical elements, background level, soils, soil pollution, guide values, Finland

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ORIGINAL PUBLICATIONS
PREFACE

The research for this thesis was carried out at the Geological Survey of Finland (GTK) during 2008–2015. The synopsis integrates six original articles dealing with different applications and uses of geochemical baselines in soil contamination assessment and other environmental decision processes. The research material was collected within the urban geochemical mapping project of GTK. This thesis focuses on practical applications and further recommendations for geochemical baselines based on literature reviews, interpretation of the statistical analysis of baseline data and scientific discussions. Applicable information is also provided for this research by individual technical reports that have been produced within the geochemical mapping projects of GTK.

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following papers:


The publications are referred to in the text by their Roman numerals.

J. Jarva’s contribution to the original publications was as follows:

I  J. Jarva had the main responsibility for data processing and the main conclusions for Paper I with the support of Dr T. Tarvainen. The geochemical baselines used for the article were collected and analysed under the urban geochemical mapping project of the Geological Survey of Finland (GTK). Mr Jussi Reinikainen contributed to the scientific basis of the soil screening values.

II J. Jarva carried out the data processing for Paper II. J. Jarva conducted the statistical analysis for the comparison between
different analytical methods with the support of Dr T. Tarvainen. Dr T. Tarvainen was responsible for the NORMA model. Mrs H. Kahelin supported the work with expertise on chemical analysis. The geochemical data used for the article were collected and analysed under the urban geochemical mapping project of GTK.

III J. Jarva had the main responsibility for planning and carrying out the study for Paper III. The geochemical data used for the article were collected and analysed under the environment geology research projects of GTK. Dr T. Tarvainen supported the selection of feasible statistical analysis and contributed to the writing. Dr P. Lintinen and Mr Juha Reini-kainen provided geochemical data and site-specific information for the paper.

IV J. Jarva had the main responsibility for carrying out the presented statistical analysis of the TAPIR data and writing Paper IV. Dr T. Tarvainen supported the selection of feasible statistical analysis. Mr Jussi Reinikainen contributed to the writing of legislative background and applications of guideline values. Mr M. Eklund had performed the background studies for geochemical provinces within his Master’s Thesis. The geochemical data used for the article were collected and analysed under the urban geochemical mapping project of GTK and are available via the TAPIR database maintained by GTK.

V J. Jarva and Dr T. Tarvainen were equally responsible in writing and explaining the practices in using information on geochemical baselines in the assessment soil contamination in Finland in Paper V. The geochemical data used for the article were collected and analysed under the urban geochemical mapping project of GTK. The Ministry of the Environment gave permission to publish the scheme on the main steps of soil contamination assessment in Finland.

VI J. Jarva had the main responsibility for planning and carrying out the study for Paper VI. Dr R.T. Ottesen supported the work with his wide experience in urban geochemical studies in Norway and internationally. Dr T. Tarvainen supported the selection of feasible statistical analysis and contributed to the interpretation of the results. The geochemical data used for the article were collected and analysed under the urban geochemical mapping of GTK. Concentrated nitric acid (HNO₃) leach based analysis was performed and offered by the laboratory of the Geological Survey of Norway. The statistical analysis and research were funded by the Academy of Finland.
1 INTRODUCTION

The world’s population is growing, and more and more people are expected to live in an urban environment in the near future. According to the United Nations (2012), the world’s population was ca. 6.9 billion in 2010, and it will grow from 8.0 billion in 2025 to 9.5 billion in 2050. At the same time, the urban population will increase. In 2014, 53.6% of the world’s population was considered as urban. It is estimated that by 2025, 58.2% of people will live in urban areas and in 2050 nearly 67% of the world’s population will be urban. In Europe, the expected growth in the urban population will be from 73.4% in 2014 to 82% in 2050, and in Finland respectively from 84.1% to 89.1% (United Nations 2014). The direct impact of urbanization is more intensive land use with strong industrial and economic activities. Since urban soils are identified as important recipients of pollutants from a number of sources such as road traffic, industry and waste incineration (e.g. Albanese & Breward 2011), the increasing anthropogenic activities may also sometimes lead to soil contamination. The growing demand to increase sustainable land management in urban areas is associated with various applications of geochemical surveys.

Soil contamination was acknowledged as a foremost environmental problem in the industrialized countries in the 1980s. This was also true in Finland (Assmuth et al. 1990). Thus, in 1988, the Government of Finland highlighted the importance of studying the level of contamination of surficial deposits and assessing their remediation needs. The Ministry of the Environment of Finland established an internal contaminated soil survey and remediation project in order to map the contaminated sites in Finland and to recommend appropriate remediation methods when necessary (Puolanne et al. 1994).

The geochemical baseline concentration is a crucial factor while assessing soil contamination. Johnson & Demetriades (2011) have acknowledged the importance of the urban geochemical baseline as follows: “Once we have defined the urban geochemical baseline, then we can monitor it for future changes, understand the sources of contamination and, with epidemiological and human health data, have a better understanding of the chemical elements and their compounds that damage our health.”

In the following, a brief overview on the development of the guidelines and legislation related to soil contamination in Finland is provided, with the main focus on geochemical baselines. The use of geochemical baseline surveys in the assessment soil contamination in Finland and in some other countries is briefly discussed and the current practices in Finland are presented. Finally, the geochemical baselines in the assessment of soil contamination in Finland are outlined with suggestions for further applications and recommendations for future research needs.

1.1 Terminology

1.1.1 Geochemical baseline

The term “geochemical background” has been used in mineral exploration geochemistry and was defined, for example, by Hawkes & Webb (1962) as “the normal abundance of an element in barren earth material.” They also pointed out that in addition, reflecting the element composition
of the underlying bedrock, the background composition of residual soil is also subject to soil type variation and soil horizon characteristics.

The term “geochemical baseline” was officially introduced in the context of the International Geoscience Programme (IGCP) project Global Geochemical Baselines in 1993 (Darnley et al. 1995). However, Tidball et al. (1974) already used the term “baseline” in a geochemical context and defined it to be based on the central 95% of recorded element concentration values. Later, Tidball & Ebens (1976) defined a geochemical baseline more hypothetically as “a collection of data points each defined as the natural value of a given geochemical measurement in a given sample that one would expect in the absence of man-induced alteration.” This definition excludes the anthropogenic input when determining the baseline. Salminen & Gregorauskienė (2000) have concluded that the definition of a geochemical baseline takes into account basic geological aspects, but also anthropogenic influences. They also highlighted how the selection of sampling media allows the determination of the geochemical baseline without any anthropogenic input. Albanese et al. (2008) pointed out the difficulty in determining the geogenic background value of an element in an urban soil due to the diffuse nature of pollution in the urban environment. They suggested the definition of two baselines for urban areas: the regional anomaly threshold, related to the background concentration interval, and the local anomaly threshold, referring not only to the geochemical background concentration but also to diffuse urban pollution. The challenge in defining the geochemical baseline was also acknowledged by Salminen & Tarvainen (2008) when they discussed regional and local variety in natural background concentrations due to differences in the type and genesis of overburden, but also due to the analytical methods and particle-size fraction used in investigations.

The usage of the terms “baseline” and “background” has been recognized to be misleading in some contexts (e.g. Reimann & Garrett 2005, Garret et al. 2008). The term “natural background” is widely used to indicate background levels reflecting natural processes uninfluenced by human activities (Reimann & Garrett 2005), while the term “baseline” is often used to refer both to the natural geological background concentrations and the diffuse anthropogenic input of substances at the regional scale. According to Johnson & Demetriades (2011), “a geochemical baseline simply reports the chemical state of the surface environment, exactly as it is, with no interpretation or partitioning of the data.” Thus, it is a concentration that is determined from a given sample of a certain geological material, with a particular method at a specific point of time (e.g. Salminen & Tarvainen 1999, Garret et al. 2008, Johnson & Demetriades 2011). Johnson & Demetriades (2011) also express “urban baseline” with a simple equation of the sum of the natural background concentration and the anthropogenic contribution. Garret et al. (2008) highlight that “it is important in environmental and ecological contexts to recognize that what has to be established are the scales and range of natural or ambient background (or baseline) variation in different environments across the Earth’s terrestrial surface.”

Thornton (1991) was one of the first to start using the term “urban geochemistry” in connection with the metal contamination of soils in urban areas. He pointed out how the chemistry of pollutants in urban soils is little understood, and the behavior of chemicals in these soils must be studied. He also raised a question and brought out his worry concerning how contaminants interact with urban soil constituents and whether this affects their behavior. Thornton (1991) also questioned how threshold or trigger values could be defined for urban soil in the case of soil contamination and remediation actions.

The urgent need for data on geochemical baselines was highlighted by European geochemists while environmental authorities were more extensively starting to define limits for levels of contaminants in soils used for different purposes in most European countries (e.g. Salminen et al. 1998). The question of how to take natural background concentrations into account while defining action limits or guideline values requires close cooperation between experts, policy makers and other stakeholders. This is nowadays well acknowledged, and many good practices and examples exist in relation to soil quality criteria that take the geochemical background into account, e.g. in Norway (Statens forurensningstilsyn 1999, Norwegian Pollution Control Authority 1999), Finland (Ministry of the Environment...
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2007, 2014a), Sweden (Naturvårdsverket 2009) and the UK (Environment Agency 2009).

1.1.2 Soil

Term “soil” holds various definitions (Reimann et al. 2014b). The Glossary of Geology (Neuen-dorf et al. 2005, 2011) describes soil as “the unconsolidated mineral or organic material on the immediate surface of the earth that serves as a natural medium for the growth of land plants.” The broad description also pays attention to effects on the climate and organisms and the altering of many physical, chemical, biological, and morphological properties and characteristics. The INSPIRE Directive (2007/2/EC) specifies soil (D2.8.III.3) as “the upper part of the earth’s crust, formed by mineral particles, organic matter, water, air and living organisms. It is the interface between rock, air and water which hosts most of the biosphere.” Furthermore, the EU Directive on Industrial Emissions (2010/75/EU) describes soil as “the top layer of the Earth’s crust situated between the bedrock and the surface. The soil is composed of mineral particles, organic matter, water, air and living organisms.” The two latter examples follow the definitions of soil given by the Thematic Strategy for Soil Protection (COM/2006/0231).

While the term “soil” in geological research often only refers to the immediate surface of the earth, many other applications uses the term in a much wider sense, covering all material between the bedrock and earth surface. This is also true in many environmental applications. In this thesis, “soil” is used to define the immediate surface of the earth, which includes the organic soil layer and the uppermost organic-mineral layer. However, when necessary, the meaning of soil follows the existing practices of the study in question.

1.1.3 Other terminology used in this research

Background concentration refers to the background levels of elements reflecting natural processes uninfluenced by human activities.

Baseline concentration refers to both the natural geological background concentrations and the diffuse anthropogenic input of substances at the regional scale, often referred to as the baseline or the geochemical baseline.

Guideline value is a concentration level for harmful elements or compounds, which when exceeded creates a need for remediation or other risk management actions.

Humus is the upper natural organic matter-containing layer, mainly of podzolised soils. It is commonly referred to as the O horizon.

ICP-AES, or inductively coupled plasma atomic emission spectroscopy, is an analytical technique used for the detection of trace elements. ICP-MS, or inductively coupled plasma mass spectroscopy, is an analytical technique used for the detection of trace elements.

Man-made soil is an occasionally used term for a soil layer or soil parent material that has been formed or heavily modified by human activity.

Near-total leach or partial leach refers to aqua regia (AR) leach or concentrated nitric acid (HNO$_3$) leach followed by ICP-AES/MS. According to Sandström et al. (2005) in the environmental chemistry, term “near–total”, is often used to describe the maximum concentration of an element that can be liberated from a material in its natural environment. An aqua regia leach is commonly used for simulating this characteristic in the laboratory.

Organic soil is the upper layer of soil, which could be comprised of natural humus or a mixture of roots, leaves and compost in man–made soil material. It is sometimes referred to as the O horizon.

Podzol is the most common soil in Finland (56%) (Yli–Halla & Mokma 2002), and podzolisation is the principal soil forming process in the forested soils in Finland (Aaltonen 1952). Typically, podzol is comprised of O (organic), A (eluvial), B (illuvial, enrichment) and C (parent material) horizons in Finland.

Weak leach refers to 1M ammonium acetate (pH 4.5) leach (often with EDTA) followed by ICP-AES/MS. Typically used to indicate highly mobile or bioaccessible concentrations.

Soil screening value is a concentration level of a harmful element or compound, which when exceeded may create the need for risk assessment and risk management.

Subsoil refers to unweathered geogenic soil parent material, and in geochemical mapping it is often a 25-cm layer within a depth range of 50–200 cm. It is commonly referred to as the C horizon.
**Surficial deposit or subsurface sediment** is the geologic deposit lying on bedrock. **Threshold value** is a concentration level of harmful elements or compounds, which when exceeded creates the need for soil contamination assessment. **Topsoil** is the uppermost mineral soil beneath any organic soil layer and is usually less than 25 cm thick. It is commonly referred to as surface soil or the A horizon.

**1.2 Development of the soil contamination guidelines and legislation in Finland**

The Ministry of the Environment of Finland published a Memorandum on “Contaminated soil site survey and remediation projects” in 1994 (Puolanne et al. 1994). It was based on studies that were carried out by the environmental authorities in 1990–1993 within the so-called SAMASE project (Saastuneiden maa–alueiden selvitys- ja kunnostusprojekti). The main aim of the SAMASE project was to investigate and propose measures for the clean-up and restoration of contaminated soils. During the project, new guideline and limit values were proposed for contaminated soils. These values were used in Finland for soil contamination assessment until 2007.

At the beginning of the SAMASE project, in 1990, preliminary national limit values were set for about 80 potentially harmful elements and substances (Puolanne et al. 1994). These limit values were mainly based on the Dutch reference values for soil quality (so-called Dutch ABC list) that were published in 1983 as a part of the Interim Soil Remediation Act by the Dutch Ministry of the Environment (e.g. Moen et al. 1986, Lamé 2010). Heikkinen (2000) compared the differences in geology and climate between Finland and the Netherlands and discussed how these differences affect the migration and sorption of harmful substances. According to the Dutch reference values, concentrations below the A value indicate that there is no soil contamination. The B value is the trigger value for soil contamination investigations and preliminary impact assessment. The C value is a limit above which extensive risk assessment and remediation is generally necessary. Today, within the framework of the Dutch Soil Protection Act, intervention values for soil remediation in the Netherlands are used to discriminate contaminated soil from cases of severe soil contamination (e.g. Rijkswaterstaat Environment 2009, Brand et al. 2012). The Finnish guidelines primarily suggested comparing investigated concentrations with the geochemical baseline concentrations of the surroundings, and secondarily with the Dutch reference values. The applicable information on geochemical baseline concentrations was to be based on already existing surveys of the Finnish environmental authorities (e.g. sludges), Agrifood Research Finland (arable land) and the Geological Survey of Finland (till). However, it was pointed out by the SAMASE working group that there was a lack of systematic geochemical baseline mapping in Finland (Puolanne et al. 1994). Existing geochemical baseline studies also had certain limitations such as diversity in the sampling media, sampling preparations and analytical methods, and they did not offer any information on the concentration levels of organic compounds. The national limit values to assess soil contamination were updated during the SAMASE project when more precise information on toxicity as well as the health and ecological impacts of elements and substances was obtained.

Local environmental conditions and land use were already noted in the SAMASE project to be taken into account in soil contamination assessment (Puolanne et al. 1994). This approach was further developed in the forthcoming guidelines.
1.3 The role of geochemical baseline concentrations in soil contamination studies

Knowledge of the natural occurrence of elements in soil deposits is necessary in determining the degree of soil pollution (e.g. Assmuth et al. 1992). Assmuth (1997) presented a more site-specific approach to defining and applying guideline values for harmful substances in soil deposits in Finland. The suggested target and guideline limit values of Assmuth (1997) were mainly based on eco-toxicological factors, but among other factors, other properties such as the organic matter and clay fraction content were also taken into account. Geochemical baselines and their role in contamination assessment were also discussed. Assmuth (1997) suggested that target values should be determined so that they are higher than the 90% fractal geochemical baseline concentration of fine-grained topsoil. In order to avoid too optimistic an approach, case-specific risk assessment with studies on bioavailability were recommended in the case of elevated concentrations of potentially harmful elements. Assmuth (1997) also pointed out that elevated geochemical baseline concentrations may additionally cause risks to human health and the environment. However, instead of remediation, minimizing the exposure is to be considered in these cases.

After the suggestions presented by Assmuth (1997), guidelines for the assessment of soil contamination were further developed by the national environmental authorities and other interest groups. In Finland, a Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) came into force on 1 June 2007. According to the Government Decree (214/2007), the assessment of soil contamination shall be based on a site-specific estimate of the risks to human health and the environment. The contamination assessment should take into account the concentrations, total amounts, properties and locations of harmful substances in the soil deposits. Natural background concentration levels should also be taken into account when assessing potential contamination and the need for remediation. This particularly applies in the case of toxic metallic elements, since background concentrations may naturally be rather high. Three categories of soil screening values, the threshold value and the lower and the upper guideline value, were introduced in the Government Decree (214/2007). The threshold value is used as a trigger value, which if exceeded indicates the necessity for further investigations on potential contamination. The geochemical baseline concentration, however, is regarded as the assessment threshold in areas with a baseline concentration higher than the threshold value. Here, the geochemical baseline concentration refers to both the natural geological background concentrations and the diffuse anthropogenic input of elements. The Government Decree (214/2007) prescribes soil screening values for 52 substances or groups of substances. The Finnish soil screening values for 11 elements and for PAH, PCB and PCDD–PCDF compounds are presented in Table 1.

The implementation of the Government Decree (214/2007) was described with specific guidelines by Ministry of the Environment (2007), which were updated in 2014 (Ministry of the Environment 2014a). According to these implementation guidelines, geochemical baseline concentrations are not only needed when assessing the potential soil contamination and remediation needs, but also in the risk assessment procedure. The geochemical baseline concentrations are recommended to take into account while defining the risk management goals and site-specific reference values for remediation.
### Table 1. Soil screening values for some potentially harmful elements and organic compounds prescribed in Appendix 1 of the Finnish Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007).

<table>
<thead>
<tr>
<th>Element</th>
<th>Background concentration (mg kg⁻¹)</th>
<th>Threshold value (mg kg⁻¹)</th>
<th>Lower guideline value (mg kg⁻¹)</th>
<th>Higher guideline value (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony (Sb) (p)</td>
<td>0.02 (0.01–0.2)</td>
<td>2</td>
<td>10 (t)</td>
<td>50 (e)</td>
</tr>
<tr>
<td>Arsenic (As) (p)</td>
<td>1 (0.1–25)</td>
<td>5</td>
<td>50 (e)</td>
<td>100 (e)</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>0.005 (&lt;0.005–0.05)</td>
<td>0.5</td>
<td>2 (e)</td>
<td>5 (e)</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.03 (0.01–0.15)</td>
<td>1</td>
<td>10 (e)</td>
<td>20 (e)</td>
</tr>
<tr>
<td>Cobalt (Co) (p)</td>
<td>8 (1–30)</td>
<td>20</td>
<td>100 (e)</td>
<td>250 (e)</td>
</tr>
<tr>
<td>Chrome (Cr)</td>
<td>31 (6–170)</td>
<td>100</td>
<td>200 (e)</td>
<td>300 (e)</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>22 (5–110)</td>
<td>100</td>
<td>150 (e)</td>
<td>200 (e)</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>5 (0.1–5)</td>
<td>60</td>
<td>200 (t)</td>
<td>750 (e)</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>17 (3–100)</td>
<td>50</td>
<td>100 (e)</td>
<td>150 (e)</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>31 (8–110)</td>
<td>200</td>
<td>250 (e)</td>
<td>400 (e)</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>38 (10–115)</td>
<td>100</td>
<td>150 (e)</td>
<td>250 (e)</td>
</tr>
<tr>
<td>PAH¹</td>
<td>15</td>
<td>30 (e)</td>
<td>100 (e)</td>
<td></td>
</tr>
<tr>
<td>PCB²</td>
<td>0.1</td>
<td>0.5 (t)</td>
<td>5 (e)</td>
<td></td>
</tr>
<tr>
<td>PCDD-PCDF-PCB³</td>
<td>0.00001</td>
<td>0.0001 (t)</td>
<td>0.0015 (e)</td>
<td></td>
</tr>
</tbody>
</table>

(p) = groundwater pollution risk should be considered  
(e) = based on ecological risk  
(t) = based on health risk

¹ Total concentration of PAH compounds includes the following compounds: anthracene, acenaphthene, acenaphthylene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, phenanthrene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, chrysene, naphthalene and pyrene.

² Total concentration of PCBs includes PCB congeners 28, 52, 101, 118, 138, 153, 180.

³ Total concentration of PCDD-PCDF-PCBs is stated as the WHO toxicity equivalent, including PCDD/F compounds and dioxin-like PCB compounds.

### 1.4 Geochemical baseline surveys in Finland

In Finland, the first geochemical surveys were carried out in the 1930s and 1940s (e.g. Rankama 1944, 1946), as described by Koljonen (1992b), and already in the late 1930s the geochemical surveys were related to mineral exploration purposes (e.g. Rankama 1940). In addition to minerogenic soil parent material, for instance Björklund (1971) also took samples from organic topsoil and birch twigs in order to identify the lead mineralization in Korsnäs, Finland. Currently, geochemical background data are available from national and regional surveys. The Geological Survey of Finland (GTK) carried out a nationwide geochemical mapping of till on a reconnaissance scale in 1983 (Koljonen 1992a) and on a regional scale during 1984–1992 (Salminen 1995). These surveys have provided information on the natural elemental distribution in till parent material, which is the most common surficial sediment type in Finland.

The Nordkalott geochemical mapping project (Bølviken et al. 1986) and the foreword of the Geochemical Atlas of Finland (Koljonen 1992a) already pointed out the usability of the knowledge on geochemical background concentrations in environmental monitoring, pollution assessment and other environmental studies, in addition to mineral exploration. It was also recognized that environmental studies would need samples not only from subsurface sediments but additionally from the topsoil. Subsurface sediment samples are good reference materials to monitor the natural state of the environment, but they do not reflect the diffuse anthropogenic input. Today, it has also become clear, especially from the urban geochemical survey point of
view, that some important trace elements such as arsenic, cadmium and lead are lacking from the analysis of previous geochemical mapping projects, or the applied analysis methods have not been able to provide sufficiently accurate measurements.

Glacial till is a mixture of local and transported mineral material and it corresponds to the composition of the bedrock. It is formed from bedrock, pre-glacial sediments and in situ weathered bedrock. Basal till is transported a short distance and represents the composition of the local bedrock, while ablation till has been carried further on top of the ice sheet. Basal till consists of finer fractions than ablation till and is almost unsorted (e.g. Salminen 1992a, Koljonen & Tanskanen 1992). Thus, basal till is commonly used for geochemical surveys targeted at mineral exploration. Regional variation exists in till properties in Finland that may affect the element distribution in till. This variation is not only due to elemental concentrations of bedrock, but also due to the origin and other characteristics of the fine fraction of till (Lintinnen 1995). Sand and gravel are sorted by the melt water from glaciers or other flowing waters. The finest material, silt and clay, is carried as a suspension in the waters and finally deposited at the bottom of water basins. These processes greatly affect the mineral and chemical composition of different sediments. Koljonen et al. (1992) and Koljonen & Tanskanen (1992) have pointed out that coarse sorted sediments are mainly composed of quartz and feldspars and are enriched in heavy, weathering-resistant minerals, while till also contains dark mafic minerals such as micas and amphiboles. Räisänen et al. (1992) studied the chemical and physical characteristics of the fine fraction of till in a known metallogenic area in central Finland. They found that the main factor affecting the increased element concentrations in the anomalous zone is the variation in mica and clay mineral types. All these factors influence regional and areal distributions in the concentrations of elements in different soil parent materials. The composition of clays differs from the chemical composition of bedrock and reflects the environment in which they have deposited (Koljonen et al. 1992, Koljonen & Tanskanen 1992). In Finland, weathering does not play a major role in the chemical composition of clay minerals due to the short time of weathering processes.

GTK continued the geochemical mapping of Finland by examining geochemical baselines around the city of Porvoo in southern Finland using humus, topsoil and subsurface sediment samples from different soil parent materials in 2002 (Tarvainen et al. 2003). This study not only focused on the geological characteristics but also on the land use of the study area. The sampling points were located both in rural and sub-urban areas of the city of Porvoo. The geochemical mapping of the city of Porvoo was also used as a pilot study to test different sample media, sampling depths and leaching methods in geochemical baseline studies. The geochemical baseline mapping project of GTK continued around the Helsinki Metropolitan Area in 2004–2005 (Tarvainen et al. 2006), in the Satakunta Region in 2006 (Kuusisto et al. 2007), in the Pirkanmaa Region in 2006–2009 (Tarvainen 2007, Kuusisto & Tarvainen 2008, Hatakka et al. 2010a), in the Hame region in 2008–2009 (Tarvainen 2010a) and in the Helsinki Metropolitan Area in 2009–2011 (Tarvainen et al. 2013a). All of these studies provided geochemical baseline information from both rural and sub-urban areas of the municipalities and cities (Fig. 3).

Urban geochemical studies have been carried out in many countries during recent years (e.g. Johnson et al. 2011). The on-going study of geochemical baselines in Finland aims at investigating baseline concentrations of heavy metals and other trace elements around urban growth centres. During recent years, the need for information on geochemical baseline concentrations within urban areas has been acknowledged and GTK has also broadened its geochemical studies to such areas. Samples have been taken within urban centres in addition to rural and sub-urban areas (Jarva & Tarvainen 2008, Tarvainen 2010b,c, 2011, Jarva 2012, Tarvainen et al. 2013b, 2014, Hatakka et al. 2014, Taivalkoski 2015). In these studies, the samples have been taken from the areas that are actively used by the public. Thus, sampling sites are located in the central parks of the cities and municipalities, and specifically in areas where children can be in close contact with soil, i.e. day-care centres, school yards and other playgrounds (Fig. 1).
The purpose of the geochemical baseline studies in Finland is to provide information on baseline concentrations for remediation projects, land extraction, land use planning and other urban operations. They also provide information for studies on the baseline status of the environment as well as for environment impact assessment (EIA). The revised Environmental Protection Act (527/2014) implements the EU Directive on Industrial Emissions (2010/75/EU) on a national level and requires the operators to provide a baseline survey of their area in order to assess the baseline status of the soil and groundwater (Ministry of the Environment 2014b). The existing geochemical baseline information can support these surveys. The baseline information can also be applied in multidisciplinary studies such as the protection of human health. Studies on children exposure risk associated to known soil contamination have been conducted in many countries especially for lead (e.g. Mielke et al. 1983, Mielke & Reagan 1998, Taylor et al. 2013, Zahran et al. 2013) and mercury (Morisset et al. 2013), and possible relationships between high element concentrations in urban soil and male fertility has been studied (Giaccio et al. 2012). In Finland, the Finnish Food Safety Authority (Evira) and GTK have just started a preliminary desktop study on the potential exposure of children to certain potentially harmful elements from food and soil with elevated baseline concentrations (Suomi et al. 2015). The results on geochemical baseline concentrations will also contribute to the future needs of the Thematic Strategy for Soil Protection (COM/2006/0231). The overall objective of the Strategy is the protection and sustainable use of soil with guiding principles such as preventing further soil degradation and preserving its functions.

1.5 Geochemical baseline surveys in other countries

It is commonly acknowledged in soil contamination studies that reliable information on geochemical baseline concentrations is essential. Natural background concentrations may vary greatly depending on geological characteristics. Diffuse pollution may cause elevated concentrations in wide areas that in most cases could also be considered as a normal (or acceptable) geochemical baseline concentration of the environment.

Carlon (2007) published a review of methods for determining soil screening values, which are generic quality standards used to regulate land contamination in Europe. Background concentrations in the derivation of soil screening values mainly concern naturally occurring substances. Natural background values have influenced the determination of target values for example in Belgium, the Netherlands and Finland. In some
countries, the soil screening values indicating negligible risk are related to geochemical baseline concentrations, either for contaminants of natural origin or diffuse contamination.

In Norway, the geochemical background concentration refers to the concentration of a substance that is naturally present. If concentrations are greater than the defined national soil quality guidelines, it should be assessed whether the high concentration values are due to contamination or the local background (Statens forurensningstilsyn 1999, Norwegian Pollution Control Authority 1999). Generic soil quality criteria are set so that no risk to the environment or human health is posed. However, the risk assessment practices allow the development of site-specific acceptance criteria that take into account local conditions such as soil parameters and land use (Norwegian Pollution Control Authority 1999, Langedal & Ottesen 2011).

In Sweden, geochemical background levels referring the natural origin of substances or diffuse anthropogenic emissions need to be taken into account in soil contamination assessment. If the concentrations of substances at a site are at the same level or below the background level, no further investigation or remediation is needed. When a site or an area has concentrations that exceed local or regional geochemical background levels, it is assumed to be contaminated and risk assessment should be initiated (Naturvårdsverket 2002, 2009, Rosén 2010).

In Denmark, geochemical background levels are compared with measured contamination levels in soil contamination studies, and high background levels will in principal allow higher levels of the substance in remediation goals (Danish Environmental Protection Agency 2002). National background levels presented by the Danish Environmental Protection Agency (Miljøstyrelsen) are provided for many of the substances, but site-specific background levels may also be detected (Danish Environmental Protection Agency 2002, Rosén 2010).

In New Zealand, background concentrations are suggested to be determined for each soil contamination investigation (New Zealand Government 2011). However, due to the unfeasibility of this type of approach, existing studies can also be used. National assessment of natural backgrounds is provided for some elements, such as cadmium and arsenic. However, data limitations have been noted, which include inadequate geographical coverage and a lack of investigations on variation in soil parent types.

In Canada, naturally occurring elements with high local natural background concentrations are considered and site-specific guidelines involving site-specific assessment are recommended (CCME 2006, 2007).

In England and Wales, methodology for the determination of normal background concentrations of contaminants in soil has been developed (Ander et al. 2013). This approach has similar factors and elements to the current practices in determining geochemical baselines in Finland as described by Reinikainen (2007) and in Paper I and Paper IV. The used term “normal background concentration (NBC)” refers to both geoegenic and diffuse sources of elements and substances that are defined as contaminants. The spatial distribution of the selected contaminants has been studied, and NBCs are determined for the most important specific areas called “domains”. These domains could be compared to geochemical provinces introduced in the national geochemical baseline database of Finland (TAPIR – taustapitoisuusrekisteri) in Paper IV. The domains, however, have a slightly more sophisticated approach. They are delineated according to three main factors: the soil parent material, urbanization degree and non-ferrous mineralization and associated mining activities. The area outside of any defined domain is called “the principal domain”. Domains are separately determined for six elements (As, Cd, Cu, Hg, Ni and Pb) and one organic substance, benzo[a]-pyrene (BaP). NBCs are determined for each element/substance and domain is based on the 95th percentile of the analysed concentrations (Ander et al. 2013).

1.6 Land use-based soil screening values in soil contamination assessment

Aquifers and their protection have played a major role in the assessment of soil contamination in Finland (Puolanne et al. 1994). In the SAMASE project, the location of contaminated sites was
analysed and evaluated according to their distance from water intakes. Land use changes, i.e. when old industrial or commercial areas are changed to residential areas, are the most common situation when soil contamination assessment is carried out. The re-use of these so-called brownfield areas has been the starting point for soil contamination studies in many industrialized countries. In the SAMASE project, the preliminary risk assessment was carried out for the identified, potential or observed contaminated sites in Finland. In order to prevent any risks posed by soil contamination, sites with low or insignificant contamination were also registered. This was additionally intended to assist land use planning actions in the future.

Land use-based soil screening values and their use in other countries were discussed by Assmuth (1997). Assmuth (1997) suggested that land use-based exposure and risk level estimations should also be included in site-specific risk assessment and remediation plans in Finland. It has been pointed out by Assmuth (1997) that elevated geochemical baseline concentrations could additionally pose a risk to human health or the environment. Here, Assmuth (1997) highlighted radon and asbestos. Again, site-specific risk assessment and risk management measures were suggested. In order to set environmentally sustainable and health-protective goals for remediation when elevated baseline concentrations may pose a risk, the minimization of exposure or reduction of damage should be considered.

Currently, the Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) describes the guideline values for potential soil contamination. The guideline values, referring to significant risks to human health or the soil ecosystem, are used as tools in the assessment. The upper guideline values are applied at industrial or similar insensitive sites and the lower guideline values in the case of other, more sensitive land use (Reinikainen 2007). In many European countries, soil screening values for soil contamination assessment are land use specific (e.g. Carlon 2007).

In Norway, soil quality guidelines for the most sensitive land uses form the basis for soil contamination assessment. In the first step, when soil contamination is suspected, detected concentrations are compared with these generic soil quality values. It must be assessed whether the concentrations that exceed the acceptance criteria are due to the contaminant or natural background levels. If soil quality guidelines are exceeded, site-specific risk assessment should take place. This phase of assessment allows the adjustment of soil quality guidelines to the current land use (Statens forurensningstilsyn 1999, Norwegian Pollution Control Authority 1999). For example, in Trondheim, the city has even established local land use-based soil quality criteria. These are based on health risk evaluation developed by the Norwegian Institute of Public Health (Folkehelseinstituttet), and on city-specific concentrations in urban soil and geochemical background concentrations (Langedal & Ottesen 2011). In Norway, even special guideline limits for acceptable concentrations of pollutants for the soil in kindergartens, playgrounds and schools are developed by the Norwegian Institute of Public Health (Alexander 2006, Ottesen et al. 2007).

In Sweden, soil quality criteria are provided for two types of land use: sensitive and less sensitive uses. Sensitive land use refers to areas that require the highest protection for humans and the environment, and can support all types of utilisation of the ground (Naturvårdsförbundet 2009, Rosén 2010). The Swedish Environmental Protection Agency (Naturvårdsverket) has recommended generic guideline values that apply throughout Sweden. Guideline values are given for both sensitive and less sensitive land uses. In cases where generic guideline values are not useful or applicable to the conditions at a contaminated site, site-specific guideline values can be determined, taking into account the actual site conditions. Site-specific guidelines, however, cannot be lower than the background levels (Naturvårdsverket 2009).

In Denmark, three categories for land use exist that are considered in soil contamination studies: highly sensitive land use, sensitive land use and non-sensitive land use. Highly sensitive land use includes farming and gardening, and also kindergartens. Sensitive land use includes parks and park-like areas, and non-sensitive land use comprises land that is used for industry and other non-sensitive activities. The Danish guideline values set a secure level of contamination at which no negative effects will occur
for recipients. Four different criteria exist: soil quality, cut-off, groundwater quality and evaporation quality criteria (Rosén 2010, Miljøstyrelsen 2014). All quality criteria are set for highly sensitive land use. Soil quality criteria are set for the protection of human health, mainly the direct exposure of children. Eco-toxicological soil quality criteria and corresponding background levels for a selection of substances are also available. The cut-off criteria state the level of soil contamination at which no contact with the upper soil can be allowed in the current or planned land use and when it is necessary to prevent all contact with the soil. In Denmark, no site-specific limit values are provided, but site-specific assessment with a special focus on exposure is conducted (Danish Environmental Protection Agency 2002, Rosén 2010, Miljøstyrelsen 2014).

The decision making and actions related to soil contamination are enacted by several pieces of legislation in Finland. The main statute is the Environmental Protection Act (527/2014), which issues prohibition of soil and groundwater contamination, as well as the duty to treat soil and groundwater in case of contamination. The Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) lays down the provisions for the assessment of soil contamination and remediation needs. The Land Use and Building Act (132/1999) promotes a safe, healthy, pleasant, socially functional living and working environment. The Act (132/1999) does not have any regulations on the content requirements of the various plans in case of potential contamination, but soil contamination usually sets limitations on land use that should be taken into account in land use planning and construction activities (e.g. Ministry of the Environment 2014a). The Association of Finnish Local and Regional Authorities has published guidelines for local authorities to support the implementation of the National Building Code of Finland (Suomen Kuntaliitto 2013). The constructor could be put under an obligation to conduct detailed soil contamination studies. The results of such studies and the possible need for actions such as remediation should be pointed out in the building permit documents. Elevated geochemical baseline concentrations are also discussed in the guidelines, but the focus is on groundwater quality (arsenic, radon) and on respiratory air quality (radon). Contaminated sites may also be subject to restrictions on use, i.e. a contaminated area may be considered unsuitable for any sensitive land use, and any changes in current land use will require an updated assessment of remediation needs.

In Finland, the licensing and supervisory authorities operating within soil contamination control are the regional Centres for Economic Development, Transport and the Environment (so-called ELY centres) and the municipal environment institutes operating in Helsinki and Turku. For environmental permits that are required in some specific cases related to soil remediation, the regional state administration agencies act as the responsible authority.

2 CURRENT PRACTICES IN FINLAND

To support the proper consideration of geochemical baselines in soil contamination studies, GTK has introduced regional baseline concentrations for pre-described geographical regions, referred to as geochemical provinces, which were originally delineated by Eklund (2008). Based on studies by Eklund (2008), seven geochemical baseline provinces where several metals (Co, Cr, Cu, Ni, V and Zn) showed anomalous concentrations have been formed (Fig. 2a). In addition, four geochemical baseline provinces for arsenic have been delineated (Fig. 2b). The geochemical statistics for these provinces are discussed in more detail in Paper IV. This rough delineation of geochemical provinces has proven to be a useful tool for preliminary soil contamination assessment. It enables the elevated concentrations to be considered as geogenic in origin if such doubts are presented. Besides the pre-defined geochemical provinces, the upper limit of geochemical baseline variation for potentially harmful elements is used for estimating the baseline concentration, as described in Papers IV and V. This parameter is suggested in Annex B of the ISO 19258:2005 standard to be used to detect the outliers of
The upper limit of geochemical baseline variation for element X (ULBL\textsubscript{X}) is calculated as follows:

\[ \text{ULBL}_{X} = P_{75} + 1.5 \times (P_{75} - P_{25}) \]

where \( P_{75} \) is the 75\textsuperscript{th} percentile and \( P_{25} \) is the 25\textsuperscript{th} percentile of element X concentrations.

Natural background concentrations are provided for the whole of Finland with various sampling densities. The previously performed till geochemical studies provide information on element concentrations in till parent material covering potentially harmful elements that are also relevant from the mineral exploration point of view (e.g. Co, Cr, Cu, Ni, V and Zn) (Bølviken et al. 1986, Koljonen 1992c, Salminen 1995). Geochemical mapping surveys in the Barents region (Reimann et al. 1998, Salminen et al. 2004) continuing to the European scale (Salminen et al. 2005) have also provided information on background concentrations from other soil horizons than only subsoil and other sampling materials. Geochemical surveys on arable land have been carried out within the Baltic Sea Region (Reimann et al. 2003), as well as at the European scale (Reimann et al. 2014a). Table 2 summarizes some reconnaissance and regional-scale geochemical mapping projects carried out in Finland.

Fig. 2. a) Geochemical baseline provinces for metals. 1 = Southern Finland metal province; 2 = Varkaus metal province; 3 = Northeastern metal province; 4 = Oulainen metal province; 5 = Kemi metal province; 6 = Lapland metal province; 7 = Enontekiö metal province. b) Geochemical baseline provinces for arsenic. 1 = Southern Finland arsenic province; 2 = Ilomantsi arsenic province; 3 = Kittilä arsenic province; 4 = Southern Pirkanmaa arsenic province. Contains data from the National Land Survey of Finland and ICT Agency HALTIK. Map layout: Kirsti Keskisaari, GTK.
Table 2. Reconnaissance and regional-scale geochemical mapping projects carried out in Finland.

<table>
<thead>
<tr>
<th>Region</th>
<th>Year</th>
<th>Number of sampling sites</th>
<th>Sampling depth, sample media</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Northern Fennoscandia| 1980–1983          | 5,400 (3,150)*           | 50–60 cm (till)
|                      |                    |                          | Stream sediment        | Bølviken et al. 1986   |
|                      |                    |                          | Stream organic matter   |                         |
|                      |                    |                          | Stream moss            |                         |
| Finland              | 1982–1991          | 1,057                    | 0.5–2.0 m (till)       | Koljonen 1992           |
| Finland              | 1982–1994          | 82,062                   | 1.5 m (till)           | Salminen 1995           |
|                      |                    | 617 (191)*               | Humus                 |                         |
|                      |                    | 609 (188)*               | 0–5 cm                |                         |
|                      |                    | 609 (188)*               | B horizon             |                         |
|                      |                    | 605 (187)*               | C horizon             |                         |
| Baltic Sea Region    | 1996–1997          | 750 (66)*                | 0–25 cm (arable land)   | Reimann et al. 2003    |
|                      |                    |                          | 50–75 cm (arable land)  |                         |
| Eastern Barents Region| 2000–2001         | 1,373 (288)*             | Moss                  | Salminen et al. 2004   |
|                      |                    |                          | Topsoil (organic)     |                         |
|                      |                    |                          | C horizon             |                         |
|                      |                    |                          | Stream water           |                         |
|                      |                    | 790 (65)*                | 0–25 cm               |                         |
|                      |                    |                          | C horizon             |                         |
|                      |                    |                          | Stream water and sediment|                        |
|                      |                    |                          | Overbank sediment (0–25 cm, bottom layer) |                  |
|                      |                    |                          | Floodplain sediment (0–25 cm, bottom layer) |                |
|                      |                    |                          | Moss                  |                         |
| Europe (GEMAS)       | 2008–2009          | 2,108 (148)*, 2,023 (41)*| 0–20 cm (ploughed land) | Reimann et al. 2014a   |
|                      |                    |                          | 0–10 cm (grazing land) |                         |

*Number of sampling sites in Finland

The geochemical studies around urban centres have also taken samples from other natural soil parent materials than till, and the selection of analysed elements has been broadened to better meet the needs of environmental applications (Peltola & Åström 2003, Tarvainen et al. 2003, 2006, 2010a,c, 2013a, Peltola 2005, Pitkäranta 2006, Kuusisto et al. 2007, Tarvainen 2007, Kuusisto & Tarvainen 2008, Hatakka et al. 2010a).

Geochemical mapping has also been carried out within the pre-described geochemical baseline provinces to collect more precise information on element distribution within these provinces (e.g. Tarvainen 2010a, Peltoniemi-Taivalkoski 2013). Figure 3 and Table 3 summarize the geochemical studies carried out around urban centres or within the pre-described geochemical baseline provinces in Finland.
Table 3. Geochemical mapping projects that have taken place at the regional scale around urban centres or within the pre-described geochemical baseline provinces in Finland. Unless indicated otherwise topsoil samples are taken from a depth of 0–25 cm and subsurface sediment samples from a 25-cm layer within a depth range of 50–200 cm.

<table>
<thead>
<tr>
<th>Region</th>
<th>Sampling year</th>
<th>Number of samples (humus - topsoil - subsoil)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porvoo</td>
<td>2002</td>
<td>80 – 130 – 130</td>
<td>Tarvainen et al. 2003</td>
</tr>
<tr>
<td>Vantaa</td>
<td>1996–1997</td>
<td>17 (humus) – 12 (0–25 cm)</td>
<td>Pitkäranta 2006, Tarvainen et al. 2013a</td>
</tr>
<tr>
<td>Vantaa</td>
<td>2006</td>
<td>11 (humus) – 6 (0–25 cm) – 10 (20–40 cm)</td>
<td>Pitkäranta 2006, Tarvainen et al. 2013a</td>
</tr>
<tr>
<td>Satakunta</td>
<td>2006</td>
<td>53 – 60 – 60</td>
<td>Kuusisto et al. 2007</td>
</tr>
<tr>
<td>Hame</td>
<td>2008-2009</td>
<td>125 – 171 – 171</td>
<td>Tarvainen 2010a</td>
</tr>
<tr>
<td>Espoo</td>
<td>2009</td>
<td>28 – 40 – 40</td>
<td>Tarvainen 2010c</td>
</tr>
</tbody>
</table>
Geochemical baseline studies within urban areas have been carried out in Finland since the 1990s. Kohonen (1994) used humus and moss samples to describe the atmospheric deposition of metals and sulphur in the city of Turku and its close surroundings. Most of the samples were impacted by diffuse atmospheric input, but single pollution sources were also possible to identify, such as the municipal waste incinerator and fuel oil heating plants. This study was followed by Salonen & Korkka-Niemi (2007), who took both organic topsoil and subsurface sediment samples from the Turku metropolitan area. Peltola & Åström (2003) and Peltola (2005) have examined the geochemical baselines within the municipality of Pietarsaari. Samples were taken from both urban and rural areas. Urban geochemical studies have also been carried out in the Tampere region (Jarva & Tarvainen 2008, Hatakka et al. 2010a) and in the cities of Espoo (Tarvainen 2010c, Jarva 2012), Rovaniemi (Taivalkoski et al. 2015), Lahti (Hatakka et al. 2014) and Heinola (Tarvainen et al. 2014). Land use targeted urban geochemical baseline studies have also been implemented, especially in the city of Helsinki (Salla 1999, 2010, Nurmi 2010, Härkönen 2010).

The University of Turku has carried out several geochemical studies in the River Kokemäenjoki delta area (e.g. Niinikoski 2011, Isotalo 2014). In these studies, in addition to river sediment sampling, reference samples have been taken from sampling pits representing the geochemical background of various subsurface sediments of the area. These results are to be utilized in future flood protection and dredging and depositing actions. Recent urban geochemical studies within urban centres in the Helsinki Metropolitan Area, Hämeenlinna and Tampere have broadened the selection of analysed elements even more to cover some precious metals (PGEs, gold) and organic compounds, and they have also targeted the sampling at areas dominated by man-made soil material (Immonen 2001, Salla 1999, 2010, Hatakka et al. 2010b, Tarvainen 2010b, 2011, Tarvainen et al. 2013a,b). Figure 4 and Table 4 summarize some of the urban geochemical studies carried out in Finland.

A European-wide urban geochemical mapping project (URGE) started in 2010. It includes the urban geochemical mapping of ten cities located in different parts of Europe. The URGE project is also utilizing the experiences of

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**Fig. 4.** The areal location of the geochemical mapping projects that have taken place within the urban centres in Finland, a) cities, municipalities and regions with urban geochemical data, b) areal distribution of sampling points in the Tampere region and the cities of Hämeenlinna, Lahti and Heinola. Contains data from the National Land Survey of Finland and ICT Agency HALTIK. Map layout: Kirsti Keskisaari, GTK.
Finnish urban geochemical mapping surveys. In Finland, the URGE project guidelines for sampling and analysis have already been used in the city of Hämeenlinna (Tarvainen 2010b, 2011). The same research methodology has also further been applied in the cities of Tampere (Tarvainen et al. 2013b), Lahti (Hatakka et al. 2014) and Heinola (Tarvainen et al. 2014), providing the city environmental administration with an urban geochemical overprint of their area.

In order to provide geochemical baseline information to be utilised in soil contamination assessment and other environmental decision processes, a national geochemical baseline database, TAPIR, was established. The TAPIR database offers scientifically sound, easily accessible and generally accepted information on the geochemical baseline concentrations in Finland. The TAPIR database is introduced in more detail in Paper IV.

The potentially contaminated and already remediated sites in Finland are registered in the soil status system (MATTI - Maaperän tilan tietojärjestelmä) maintained by the Finnish environmental authorities. In February 2013, approximately 24,000 land areas were recorded in the MATTI register (Pyy et al. 2013). The estimated total costs of investigation and remediation of these documented sites are expected to rise as high as €4 billion (Pyy et al. 2013).

In the MATTI register, the sites are classified into four classes based on the status and action needs of the site. The sites with activities that may possibly cause soil contamination and sites that require soil contamination assessment comprise nearly 75% of sites recorded in the MATTI register. Less than 10% of the recorded sites are found to be contaminated and require assessment of remediation needs and possible remediation. About 17% of recorded sites have been remediated to an acceptable level for their current purpose or have been noted to be clean. However, these sites may still include land use restrictions in the case of land use changes (Pyy et al. 2013).

The latter class within the MATTI register is closely related to risk-based remediation of contaminated soil. It is essential that the remediation levels applied are recorded for future needs. Especially in case of land use changes from less sensitive land use (e.g. industrial site) to more sensitive land use (e.g. residential area), updates may be needed in risk assessment and additional remediation may ultimately be required. For these sites with elevated concentrations, it is also possible to set restrictions for aggregate excavation and utilization off-site (Pyy et al. 2013).

Table 4. Geochemical mapping projects that have taken place within the urban centres in Finland.

<table>
<thead>
<tr>
<th>City / municipality</th>
<th>Sampling year</th>
<th>Number of samples</th>
<th>Sampling depth</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turku</td>
<td>2004</td>
<td>100</td>
<td>0–5 cm</td>
<td>Salonen &amp; Korkka-Niemi 2007</td>
</tr>
<tr>
<td>Espoo</td>
<td>2009</td>
<td>30</td>
<td>0–2 cm</td>
<td>Tarvainen 2010c, Jarva 2012</td>
</tr>
<tr>
<td>Tampere region</td>
<td>2006–2007</td>
<td>18</td>
<td>0–2 cm</td>
<td>Jarva &amp; Tarvainen 2008</td>
</tr>
<tr>
<td>Helsinki Metropolitan Area</td>
<td>2009, 2011</td>
<td>48</td>
<td>0–25 cm</td>
<td>Tarvainen et al. 2013a</td>
</tr>
<tr>
<td>Hämeenlinna</td>
<td>2010</td>
<td>40</td>
<td>0–25 cm</td>
<td>Tarvainen 2010b</td>
</tr>
<tr>
<td>Tampere</td>
<td>2012</td>
<td>195</td>
<td>0–10 cm</td>
<td>Hatakka et al. 2014</td>
</tr>
<tr>
<td>Lahti</td>
<td>2013</td>
<td>195</td>
<td>0–10 cm</td>
<td>Tarvainen et al. 2013b</td>
</tr>
<tr>
<td>Heinola</td>
<td>2013</td>
<td>161</td>
<td>0–10 cm</td>
<td>Tarvainen et al. 2014</td>
</tr>
<tr>
<td>Rovaniemi</td>
<td>2013–2014</td>
<td>100</td>
<td>0–10 cm</td>
<td>Taivalkoski et al. 2015</td>
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</table>
geochemical baseline concentrations (Ministry of the Environment 2015).

At present, the assessment of soil contamination and remediation needs according to the guidelines is to be based on the risk assessment process. This means the recognition of potentially harmful substances and the risks and threats they may cause to human health and to the environment. The remediation needs and its goals are to be based on site-specific risk assessment. However, this practice has not completely found its way to Finnish soil contamination applications. There is still a need to promote justified risk-based decisions and to increase sustainability in contaminated site remediation (Reinikainen 2014).

2.1 Implementation of geochemical baseline information in soil contamination assessment – examples from Finland

In order to attain a better overview on the practical use of geochemical baselines in soil contamination assessment, a small number of unofficial interviews have been carried out. The questions on current practices were directed to responsible environmental authorities of the city of Helsinki (A. Salla, personal communication, June 2013) and to the regional Centres for Economic Development, Transport and the Environment of Uusimaa (K. Savelainen, personal communication, October 2013) and Pirkanmaa (K. Pyötsiä, personal communication, October 2013) representing licensing and supervisory authorities concerning soil contamination in their area. The locations of these three study areas are indicated in Figure 5.

In all three cases, no official statistics exist on risk assessment or remediation projects that have been based on geochemical baseline concentrations instead of threshold or guideline values presented in the Government Decree (214/2007). However, geochemical baseline concentrations have been taken into account in soil remediation goals, even before the Government Decree (214/2007) came into force. Already in the 1990s, baseline concentrations of arsenic and vanadium in the Uusimaa region were considered to be higher than the valid soil screening values. This was especially noted in areas with clay deposits. In the city of Helsinki, one of the first examples of using baseline concentrations as a remediation goal is from 2003. In the

![Figure 5](image-url)
construction of a harbour area, elevated concentrations of arsenic were found to be geogenic in origin. The remediation goal was accepted to be based on the background level of arsenic. Some other cases with suggestions to use higher remediation goals have also been introduced to the environmental authorities of the city of Helsinki prior to the Government Decree (214/2007), but the elevated concentrations have found to be anthropogenic in origin and the plans have not been accepted. In the Pirkanmaa region, from 2003, arsenic and vanadium have been the most common elements whose baseline concentrations have been considered higher than valid soil screening values, and remediation goals have followed this presumption.

The city of Helsinki already started to map the geochemical baselines of the city area in 1996 (Salla 1999). Presently, the city is using both its own mapping results and the TAPIR database for geochemical baseline concentration estimations. Arsenic is the most common element whose baseline concentrations are typically higher than the threshold value in the area of the city of Helsinki.

In the Uusimaa region, arsenic is practically always considered to be higher than the threshold value. Vanadium and zinc also have elevated concentrations in clay deposits and are often considered to be geogenic in origin. Presently, the environmental authorities recommend the use of the TAPIR database or the existing separate geochemical baseline studies (e.g. Salla 1999, 2010, Tarvainen 2010c, Jarva 2012, Tarvainen et al. 2013a) for soil contamination assessment. Risk assessment has not been required if measured concentrations are below the regional geochemical baseline. Experience has also shown that topsoil (0–25 cm) is the most applicable material for preliminary risk assessment, especially if the contaminated site is located in an area with clay deposits.

In the Pirkanmaa region, practically all soil contamination assessments include the estimations of geochemical baseline concentrations. Arsenic and vanadium are the most common elements whose geochemical baseline concentrations in the Pirkanmaa region are often higher than the threshold value. Presently, the regional geochemical baseline information is based on the TAPIR database.

The environmental authorities have pointed out some challenges in the practical implementation of geochemical baseline concentrations in soil contamination studies. The Government Decree (214/2007) includes rather common terms in defining the geochemical baseline concentrations such as “concentrations of hazardous substances in topsoil in a wide area”. The soil screening values are defined only for some elements, and elements that are missing from the Government Decree (214/2007) are often also lacking from the contamination assessment studies. However, the Government Decree (214/2007) also requires other harmful substances than those presented in the Decree to be taken into account in the assessment of soil contamination and remediation needs. There is additionally a need for more information on the potential risks associated with certain organic compounds appearing in the living environment.

3 MATERIALS AND METHODS

3.1 Sampling and sample materials

The main sample parent material that has been used in geochemical baseline studies is minerogenic soil. In Finland, geochemical mapping surveys have traditionally used the most common soil parent material, glacial till. In order to provide geochemical baseline information on other natural soil parent materials than glacial till, the geochemical baseline mapping projects of GTK have also taken samples from sand and other coarse-grained sorted sediments, as well as from clay and other fine-grained sediments. In urban areas, the sample parent material varies greatly, ranging from relatively undisturbed natural soils to completely man-made soil with variable textures.

The organic soil layer (humus) is sometimes used in geochemical studies. The humus layer is considered to reflect both the atmospheric input
Geochemical baselines in the assessment of soil contamination in Finland and underlying geology (Kohonen & Salminen 1993, Salminen et al. 2011). The characteristics of organic layer samples vary depending on the study area. In urban areas, the organic layer is often a mixture of roots, leaves and compost under the planted grass in the park or in flowerbeds, while in sub-urban areas the organic layer often represents the natural humus layer of podzol or other forest soil. A humus sample is usually taken under the green vegetation and litter. Both sample types have also been used in the geochemical baseline mapping projects of GTK.

Vegetation is also used in some urban geochemical baseline studies. In Athens, Greece, the determination of lead and cadmium concentrations in the urban environment was based on the surveying of both soil parent material and plants (Chronopoulos et al. 1997). In Sweden, water and terrestrial moss samples were used in parallel with soil parent material during an urban geochemical mapping programme (Lax & Andersson 2011). In Oslo, Norway, terrestrial moss and different plant materials (leaves, needles, bark, wood) were used in order to identify the urban contamination footprint (Reimann et al. 2006; 2007a,b). A transect through Oslo with different sampling media was used (Reimann et al. 2011). Since terrestrial mosses indicate the atmospheric input, they have been used to map recent emissions from anthropogenic sources (e.g. Salminen et al. 2011). In Finland, snow has been used as an indicator for atmospheric input in the close vicinity to main roads (Tarvainen & Jarva 2009a).

Both composite and single samples have commonly been used in geochemical baseline studies. The selection between composite and single samples greatly depends on the main aim of the geochemical baseline study. Composite sampling is used for screening the local average level of element contents within a certain area (Gustavsson 1992). Combining several samples, however, has the ability to reduce heterogeneity and mask high concentrations (Gustavsson 1992, Ottesen et al. 2008). Composite sampling is commonly used in urban geochemical studies to indicate diffuse contamination and to map the general distribution of element concentrations. Single samples are especially used in areas with very heterogeneous conditions when the mixing of sample media could mislead the interpretation of results. At GTK, single samples were chosen for geochemical baseline studies. This was because the data were targeted to be used for calculating statistics on different soil parent materials and land use patterns. This approach also aimed at supporting environmental authorities in their decision making. Salla (1999) noted, based on the first geochemical mapping results in Helsinki, that the detected urban geochemical baselines displayed significant variation, and areas with similar characteristics could not be identified within the city. This was mainly due to considerable variety in the soil parent material.

The selection of the sampling grid has varied among urban geochemical baseline studies, and both systematic and targeted surveys have been used (Johnson & Demetriades 2011). In systematic surveys, a sampling grid with a particular size is used and sampling does not target or avoid any areas, such as sites with known or suspected contamination (Glennon et al. 2014). The urban geochemical baseline studies of GTK are targeted. Known or suspected contamination sites are avoided and the sampling scheme takes into account both the land use and soil parent material in order to achieve as extensive an overview of the geochemical baseline variation as possible.

Selection of the appropriate sampling density is an essential part of geochemical mapping. If the sampling density is too coarse, many details may be undetected. Thus, the aim of the geochemical mapping determines the appropriate sampling density. Salminen (1992b) has divided the sequence of geochemical exploration into three phases: regional, local and detailed. In the regional phase, the sampling density is 1 sample/4 km², in the local phase the sampling density varies from 10 to 30 samples/km², and in the detailed study phase the sampling density is about 400 to 1000 samples/km². Large regional differences in geochemical background levels can be observed, even from surveys with a low sample density (Salminen 1992b, Birke et al. 2015). Low-density geochemical surveys provide a cost-effective means to assess information over large areas. However, anthropogenic influences are better detected by using high-density sampling (e.g. Birke et al. 2015). The nominal sampling density of the EuroGeoSurveys urban topsoil geochemical project (URGE) for systematically covering a town or city was set to
4 samples/km². In principle, central parts of the cities were recommended to have grid size of 500 x 500 m, and newer parts a 1000 x 1000 m grid size with less dense sampling (Demetriades & Birke 2015a, b). The density suggested by Demetriades & Birke (2015a,b) is considered to be appropriate to obtain a sufficient overview of the spatial distribution of chemical elements in urban topsoil. In the urban geochemical baseline studies of GTK, the sampling density has been 3–4 samples/km², and sampling has been concentrated in old city centres with the most intensive land use. In the geochemical mapping projects of GTK that have taken place at the regional scale around urban centres or within the pre-described geochemical baseline provinces, the sampling density has been 1 sample/10 km².

The sampling depth in geochemical mapping is traditionally quite variable, but in urban geochemical baseline studies the main focus is on topsoil (Johnson & Demetriades 2011). Topsoil is considered to give the most representative information on the concentrations in the urban environment due to its role as the main receptor of urban contamination (Mielke et al. 1999, Johnson & Demetriades 2011, Glennon et al. 2014). Especially when the land surface is not grass covered, it can increase the risk of exposure. Here, it must be noted that the material termed “topsoil” often varies from samples of the top 0–2 cm layer to 0–25 cm topsoil samples (Johnson & Demetriades 2011). During the current geochemical baseline studies at GTK, humus, topsoil (0–25 cm) and subsurface sediment samples from a 25-cm layer within a depth range of 50–200 cm were taken around urban centres or within the pre-described geochemical baseline provinces to indicate the geochemical baseline concentrations (Fig. 6). Within the urban areas, samples are nowadays taken from the upper 0–10 cm for urban geochemical baseline determination (Fig. 7).
3.2 Analytical methods

There is considerable variety in the pre-treatment and chemical analytical methods that are used in soil contamination studies, as well as in determining geochemical baselines. Total or near-total element concentrations of inorganic contaminants are determined. The samples are dried with different methods and they might be crushed and sieved to different fractions (i.e. < 2 mm, < 1 mm). And finally, in risk assessment procedures, various analytical methods are used to determine the bioavailable concentrations.

In Finland, guidelines are given for the analytical methods to be used in soil contamination assessment (Ministry of the Environment 2007, 2014a), and they are also followed in the geochemical baseline surveys of GTK. For determining inorganic elements, samples are to be sieved to the <2 mm fraction, while for determining organic compounds, the extraction is carried out from unsieved sampling material. Sample drying should be carried out in appropriate conditions taking into account the behaviour of different elements and substances. For example, mercury is easily evaporated and organic compounds may include volatiles. To determine the inorganic elements, aqua regia (AR) extraction is recommended for minerogenic material and nitric acid (HNO\(_3\)) leach for minerogenic material with a high organic matter content (humus, sludge). Aqua regia leaches carbonates and most of the sulphides. It is widely accepted in environmental sciences as providing a good estimate of the maximum potential of soluble elements in soil parent material (Niskavaara 1995). The residual elements that are not leached by aqua regia digestion are mostly bound to silicates and are often considered unimportant when estimating the mobility and behaviour of the elements (Niskavaara et al. 1997). Different gas chromatographic methods are recommended to be used to analyse organic compounds. It is recommended to use accredited or standardized analysis methods as far as possible. The concentrations are to be reported in terms of the dry matter content.

Urban geochemical surveys usually concentrate on studying the distribution of inorganic elements in the surface soil. The major elements commonly found in the urban environment are As, Pb, Zn, Ni, Hg, Cu, Cd and Cr, i.e. elements that are also identified with soil screening values within Finnish legislation (Government Decree 214/2007). Recently, it has been further noted that, for example, catalytic converters release platinum and palladium to the urban environment (e.g. Cicchella et al. 2003, Albanese et al. 2008).

In Norway, organic compounds are also systematically mapped in urban geochemical baseline studies (e.g. Ottesen et al. 1995, 1999, Haugland et al. 2008). Gas chromatography is often used in the analysis of organic compounds, but it is notable that detection limits vary greatly. The concentrations of organic compounds resulting from diffuse contamination are usually very low and close to the detection limits (e.g. Tarvainen et al. 2013a). Elevated concentrations of organic compounds are often related to point contamination sources such as PCBs from building fragments (Hellman et al. 2003, Jartun 2011), dioxins and furans from municipal solid waste incinerators (Andersson & Ottesen 2008, Andersson et al. 2011) and old sawmills with wood impregnation areas (Reinikainen 2007). However, elevated concentrations of organic compounds in urban soil may also occur due to atmospheric diffuse emissions such as PAH compounds from industry, domestic heating and vehicle emissions (Jensen et al. 2011).

In the current geochemical baseline studies at GTK, organic compounds are not systematically analysed. When organic compounds (mainly PAH and PCB compounds) have been included to the survey programme, samples for these analyses have been taken from every 10\textsuperscript{th} sampling point.

The chemical analysis chosen for the geochemical baseline study is of great importance. Many investigations use more than one analytical technique in order to obtain a wider view of the total or near-total concentrations of elements. Different analytical methods can be used to distinguish between natural and anthropogenic contamination sources, as well as for determining the bioaccessible fraction of the elements (e.g. Johnson & Demetriades 2011). For example, in Athens, Greece, both near-total and weak leaches were used while investigating the concentrations of metals in playgrounds.
Weak leach with diethylene triamine penta-acetic acid (DTPA) was used to indicate the bioavailable fraction of a metal, but it was also used to provide information on recent soil pollution.

### 3.3 Quality control in geochemical baseline studies

Quality control is essential in order to ensure that the obtained data are fit for purpose. Quality control should cover all aspects of work from the start (field sampling) to the finish (laboratory analysis) (Johnson & Demetriades 2011). Quality control is part of the quality assurance process that should be used throughout the different phases of the project in question (Johnson 2011).

In the geochemical baseline studies of GTK, sampling has been carried out by certified sampling personnel applying sampling methods that have been selected for urban geochemical mapping (Tarvainen et al. 2003, Ottesen 2009). The majority of the used chemical analysis methods are accredited (Tarvainen et al. 2003, 2013a, Hatakka et al. 2010a). Traditionally, quality control within urban geochemical mapping has included two phases: the collection of field-site duplicates for sampling quality control (mostly every 20th sample) and the use of laboratory standard samples for the control of analysis quality at regular intervals (5% at minimum). Quality control has been based on expert reviews of analysis results promoted with field recording and photographs as well as on statistical tests and on visual inspection of analytical results with boxplots or other statistical graphs. The detection limits of different sampling batches have also been reviewed (e.g. Hatakka et al. 2010a, Tarvainen et al. 2013a). In the city of Porvoo, analysis of variance (ANOVA) was also applied for field-site duplicates (Tarvainen et al. 2003), but the ANOVA method is not currently in systematic use. In recent studies, a project standard prepared by the Research Laboratory of GTK from natural glacial till from the Tampere region has also been used as part of quality control. Project standards have been included in the sample set at the same frequency as the field-site duplicates, i.e. at an average rate of one in twenty. In 2014, a Quality Control (QC) programme on the urban soil geochemical dataset was conducted in three cities of Finland, Tampere, Lahti and Heinola, where geochemical mapping was carried out with similar methods. Scatterplots, “Thompson and Howarth” plots, together with the Spearman’ s rho were used to determine the statistical acceptability of the analysis results of project standards (Fig. 8), laboratory standards (Fig. 9) and field duplicates (Figs. 10 and 11) (Guagliardi & Tarvainen 2014).
Fig. 8. Schematic diagram of zinc concentrations in the GTK project standard sample showing quality control patterns. The median value for zinc is 36.55 mg kg⁻¹ (based on aqua regia extraction of the <2 mm particle-size fraction). The project standards were analysed during three different urban geochemical mapping projects (based on Guagliardi & Tarvainen 2014).

Fig. 9. Schematic diagram of zinc concentrations in the laboratory standard sample (QCTILL4) showing quality control patterns. The median value for zinc is 57.3 mg kg⁻¹ (based on aqua regia extraction). The laboratory standards were analysed during three different urban geochemical mapping projects (based on Guagliardi & Tarvainen 2014).
Fig. 10. Scatter plot of zinc concentrations in the field duplicate samples based on aqua regia extraction of the <2 mm particle-size fraction. All data, except for a few outliers presumably due to the heterogeneity of soil pattern, are compactly distributed along the 1:1 line, indicating good repeatability of the sample grades. The analytical batches are from three different urban geochemical mapping projects (based on Guagliardi & Tarvainen 2014).

Fig. 11. “Thompson and Howarth” plot of field duplicate analysis for the zinc content (based on aqua regia extraction of the <2 mm particle-size fraction). The dashed and continuous lines respectively indicate 10% and 20% precision. The analytical batches are from three different urban geochemical mapping projects (based on Guagliardi & Tarvainen 2014).
## 4 OVERVIEW OF THE INDIVIDUAL STUDIES

The present thesis focuses on six separate research topics listed in Table 5. The table summarizes the main data sets and analytical methods applied to the data for each research topic.

Table 5. Research objectives, applied data and methods of data analysis applied in this thesis.

<table>
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<tr>
<th>ID</th>
<th>Objective</th>
<th>Data</th>
<th>Data Analysis</th>
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<tbody>
<tr>
<td>1</td>
<td>Are there any regional differences in geochemical background concentrations? (Paper I) Do the background concentrations depend on the sampling material? (Paper I)</td>
<td><strong>Sampling material</strong>: Humus samples Topsoil (0–25 cm) and subsurface sediment (subsoil) with sample media of till, sand and clay</td>
<td>Boxplots – comparing different layers (top- and subsoil) within the region Boxplots – comparing humus samples and different soil parent materials (till, sand, clay) between two regions Boxplots – showing the distribution of datasets Boxplots – comparing background concentrations with the threshold value</td>
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<td></td>
<td><strong>Analytical methods</strong>: &lt;2 mm fraction Aqua regia extraction for minerogenic samples Concentrated nitric acid leach for humus samples ICP-AES/MS</td>
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<td>2</td>
<td>What is the significance of the differences between commonly used determinations and analytical methods in geochemical baseline studies in geologically varied areas? (Paper II)</td>
<td><strong>Sampling material</strong>: Topsoil (0–25 cm) and subsurface sediment (subsoil) samples with sample media of till, sand and clay</td>
<td>ANOVA – quality control Scatter diagrams – comparing concentrations in different soil parent materials using different analytical methods NORMA model – determination of mineralogical composition of samples; showing the difference in geology in two study areas Wilcoxon’s signed rank test – indicating the significance of the differences between studied geochemical baseline concentrations in different soil parent material determined using aqua regia extraction and concentrated nitric acid leaching. The median ratio – comparing different analytical methods and solubility of elements</td>
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<td><strong>Analytical methods</strong>: &lt;2 mm fraction XRF or strong acid leach (total) Aqua regia extraction or concentrated nitric acid leach (near-total) ICP-AES/MS</td>
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<td>ID</td>
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| 3  | Is it possible to carry out simplified chemical characterization of metal-contaminated soil? (Paper III) How can we separate the site-specific metal contamination from the elevated geochemical baseline concentrations? (Paper III) | **Sampling material:** Topsoil and subsurface sediment samples (subsoil)  
**Analytical methods:** <2 mm fraction  
Aqua regia extraction  
Acid ammonium acetate leach  
Synthetic rainwater leach  
De-ionised water leach  
ICP-AES/MS | Comparison of concentrations with the geochemical baselines and Finnish soil screening values  
Boxplots – showing the distribution of elements at different sample depths  
Leachability – determining the ratio between ammonium acetate and aqua regia extractable concentrations  
Cluster analysis – characterization of the soil parent material, sources of elements and potential contamination  
Factor analysis – characterization of the soil parent material, sources of elements and potential contamination |
| 4  | How can the nationwide soil geochemical baseline data be applied in decision making? (Paper IV) | Data clustering by identified geochemical provinces  
National geochemical baseline database (TAPIR) | Kolmogorov-Smirnov test – testing the cumulative distribution of pre-defined geochemical provinces  
Mann-Whitney test – testing medians of pre-defined geochemical provinces  
QQ-plots and beanplots – visualizing the difference between pre-defined geochemical provinces  
Calculation of the upper limit of baseline variation |
| 5  | How can the geochemical baseline data be applied in the assessment of soil contamination at regional and local levels? (Paper V) | Regional geochemical baseline studies  
Calculation of the upper limit of baseline variation |
| 6  | What is the representative sampling depth for geochemical baseline studies in urban areas? (Paper VI) | **Sampling material:** Topsoil samples (0–2 cm and 0–25 cm) from urban soil (two commonly used sampling depths)  
**Analytical methods:** <2 mm fraction  
Aqua regia extraction  
Concentrated nitric acid leach  
ICP-AES/MS | Bean plots and boxplots – comparing two sample depths; showing the distribution of datasets  
Scatter diagrams – comparing different analytical methods  
Statistical tests – indicating the significance of the differences between two sample depths and analytical methods |
Paper I. Based on the previous and on-going geochemical studies in Finland, the natural variation in background concentrations is generally rather significant. Geochemical background concentrations of two regions, Satakunta and Pirkanmaa, are discussed in Paper I with the focus on arsenic. The regional differences in geochemical background concentrations and influence of sample material on concentrations were investigated (research objective 1 in Table 5). The measured background concentrations were compared to threshold values described by the Finnish Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007).

When comparing arsenic concentrations between two regions, the regional difference in concentration levels was clearly detected in minerogenic soil parent material. The arsenic concentrations were notably higher in the Pirkanmaa Region than in Satakunta. The considerable variability in arsenic concentrations between two regions illustrates the importance of information on regional geochemical background concentrations while assessing potential soil contamination. Thus, in order to distinguish actual contamination from background or baseline concentrations and to identify regional differences due to geological characteristics, geochemical baseline studies provide substantial information.

The soil screening values prescribed in the Government Decree (214/2007) are grounded in various risk-based reference values considering ecological risks, health risks and risks to groundwater quality. For arsenic, the threshold value of 5 mg kg⁻¹ is mainly based on the potential risk from groundwater contamination and the lower guideline value of 50 mg As kg⁻¹ is based on the ecological reference value. The upper guideline value of 100 mg As kg⁻¹ was set based on arsenic toxicity to terrestrial species. The studied reference values representing significant health risks from arsenic were higher than the corresponding ecological values and did not therefore contribute to the Finnish guideline values for arsenic.

In the Pirkanmaa Region, differences in soil type do not significantly affect the concentrations of arsenic, while in the Satakunta Region the arsenic concentrations in fine-grained sediments were higher than in coarser-grained soil parent materials. In the humus layer, no difference in arsenic concentrations was identified between the two regions. The studied geochemical background concentrations of arsenic in Satakunta and Pirkanmaa were below the Finnish guideline values in all sampling media. Threshold value was exceeded in Pirkanmaa which should be taken into account in soil contamination studies.


Paper II. In Finland, the analytical methods recommended for use while investigating possible soil contamination are specified, and either aqua regia extraction or the concentrated nitric acid leach method are suggested for metals and metalloids. The same analytical methods are also used in geochemical baseline studies. In addition to these, total analyses (XRF) and total leach (4-Acid Leach) are also used in geochemical mapping. Paper II compares trace element concentrations analysed with these commonly used analytical methods in geochemical baseline studies (research objective 2 in Table 5). Statistical tests indicate that aqua regia and concentrated nitric acid digestions reveal differences for some elements (e.g. As, Pb and Sb) between the two analytical methods when measuring geochemical baseline concentrations, i.e. relatively low concentrations in soil deposits. The detection limits of these two methods may differ, and especially when assessing low geochemical baseline concentrations this should be carefully considered.

The studies showed that the significance of differences between total and near-total concentrations is high for all studied elements. While the soil screening values are defined for near-total concentrations in the Finnish legislation, the total concentration determined by XRF cannot be used instead of strong acid digestion results in non-contaminated areas while assessing regional geochemical baselines. Paper II also remarks that comprehensive risk assessment studies additionally require information on element concentrations based on sequential extractions.
Two regions, Itä-Uusimaa (mainly Porvoo region) and Pirkanmaa (mainly Tampere region), with different geological environments were selected for the study (see Fig. 3 for locations of study regions). The NORMA model was used to estimate the normative mineralogical composition of samples collected. The differences in regional geochemical baselines are partly explained by the abundance of micas and secondary minerals. Concentrations of Sb, Cd, Co, Cr, Cu, Ni, Pb, V and Zn in topsoil are strongly correlated with the content of normative biotite and chlorite. The comparison demonstrated that near-total concentrations of several elements were strongly controlled by the abundance of micas, goethite and hydrous Al-silicates, and the organic carbon content was strongly correlated with some elements.


Paper III. Two study areas representing contaminated land were compared with regional geochemical baselines using various analytical methods: aqua regia extraction, concentrated nitric acid leach, ammonium acetate extraction and synthetic rainwater or distilled, de-ionised water extraction in Paper III (research objective 3 in Table 5). The same metals that showed enrichment compared to the geochemical baselines often had elevated leachability to ammonium acetate (research objective 3 in Table 5). It can be assumed that these elements are also more bioavailable in contaminated land and can therefore pose a risk to the environment. The vast majority of the investigated samples showed very limited metal solubility to waters. However, in a single sample representing high contamination, both ammonium acetate and water extractable concentrations were high. The combination of various analytical methods revealed the heterogeneity of the man-made soil material. Studies of this kind on the potential leachability of elements are of great importance in the risk assessment of contaminated land.

Study area 1 of Paper III represented an area with entirely man-made soil material. In study area 1, Co, Cr, Ni and V concentrations were of the same order of magnitude as the regional geochemical baseline levels, while Cu, Hg, Pb and Zn showed general enrichment and potential pollution.

Study area 2 of Paper III represented an area with less than 1 m anthropogenic soil covering undisturbed glaciofluvial sediments. In study area 2, Co, Cr, Ni, V and As concentrations were within the regional geochemical baseline levels, while Cu, Hg, Pb, Zn, Sb and Cd showed general enrichment as well as a few hotspot concentrations. The highest concentrations were found in the upper 25 cm. The studies on groundwater supported the estimations of soil contamination in study area 2.

The ratio between ammonium acetate (AA) and aqua regia (AR) extractable concentrations was determined in order to estimate the potential overall leachability of selected elements in (man-made) soil deposits of two study areas. In addition, the ratio between water (W) and aqua regia extractable concentrations was studied. The solubility based on AA/AR ratio was generally higher in contaminated soil than those from geochemical baseline studies. Some elements in contaminated soils were found to be slightly soluble in water. In general, concentrations based on water leach were below the detection limits.

Cluster analysis illustrated with dendrograms was found to be a feasible tool for characterizing contaminated soil. With a sufficient number of samples and an appropriate sampling density, the geochemical classification of contaminated soil could be carried out using dendrograms. In study area 1, separate clusters with high metal contamination were possible to identify. However, the scattered sampling density hindered any specific analysis of fill material character. In study area 2, the elements with median concentrations similar to the geochemical baseline level could be distinguished from those with general enrichment due to anthropogenic activities. On the other hand, the clusters were able to distinguish the most leachable elements. Thus, cluster analysis could also be used to make a preliminary assessment of the nature of the potential contamination. Together with cluster analysis, factor analysis can help to recognize
different groups of chemical elements with the same geochemical pattern. Different factors can also be used to interpret the origin of elements under investigations.


Paper IV. Finnish national geochemical baseline database, TAPIR, is introduced in Paper IV. The general background, structure and content of TAPIR are explained. In addition, the principle for determining the maximum acceptable baseline concentration for a geochemical province is introduced.

According to Paper IV, the pre-defined geochemical provinces presented in TAPIR can be used while estimating the geochemical baselines for sand deposits and especially for glacial tills. The upper limit of the baseline concentration based on the 25th and 75th percentile is a robust estimate for the regional geochemical baseline concentration. However, geochemical baselines of fine-grained sediments do not necessarily follow the distribution of these geochemical provinces. Geochemical baseline data are still very scarce for many essential trace elements such as As, Cd, Hg, Pb or Sb. However, the national database, which combines data from various data producers, provides the means to gather information on all soil parent materials and all provinces in a reasonable time and limits the costs for such a national inventory. Paper IV suggests that the delineation of the pre-defined geochemical provinces should be revised and the upper limit of the baseline variations within geochemical provinces should be recalculated after more analytical information is available for the database.

Paper IV brings out that reliable data on the geochemical baselines is of special importance from the viewpoint of decision makers, authorities and site owners in regions where the geochemical baselines may exceed the threshold values given in the Finnish Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) (research objective 4 in Table 5). Reliable information on geochemical baselines enables case-specific guidelines for soil contamination assessment to be determined. If regional geochemical baseline values are available, the guideline values based on ecological risks can be modified accordingly. The recalculations of regional guideline values will give tools to better assess the remediation needs as well as to choose the best available remediation technique for the area in question.


Paper V. An example of applying geochemical baseline data is presented in Paper V. Studies on geochemical baselines have revealed considerable natural variation in trace-element concentrations throughout Europe. Assessment of soil contamination cannot be performed without prior knowledge of geochemical baseline concentrations. Usually, all soil screening values are based on various risk-based reference values. Assessment of soil contamination without information on geochemical baselines can therefore lead to unnecessary risk calculations and even to costly remediation actions.

In Finland, a Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) gives the possibility to use geochemical baselines in soil contamination assessment. Paper V introduces the main steps of soil contamination assessment in Finland and provides practical examples of geochemical baselines in a region with naturally elevated arsenic concentrations. Paper V discusses the principles of the upper limit of baseline variation within a geochemical province (research objective 5 in Table 5). The need for identification of local geochemical provinces for geological anomalies (mineralisations) and anthropogenic hot spots (urbanized areas) is also highlighted.

Paper VI. The importance of sampling depth in urban geochemical studies is discussed in Paper VI. Two sample depths, 0–2 and 0–25 cm, were chosen for the study. Statistical analysis revealed that element concentrations for the two studied sample depths were different for most of the studied elements. This demonstrated that urban surface soil appears to be very heterogeneous and elements are not evenly distributed vertically. For most studied elements, the median concentrations were higher in the 0–25 cm samples, but large variation in concentrations was found in the topmost 0–2 cm layer. The difference between concentrations in urban soils of different layers was mostly seen with elevated Pb concentrations in the 0–2 cm layer near main roads. This study did not conclusively establish whether a sampling depth of 0–2 or 0–25 cm should be recommended for similar studies in the future. The selection of the sampling depth in geochemical studies greatly depends on the aims of the project. This study demonstrated that even in urban surface soils that are mainly man-made in origin, the 0–25 samples were more homogeneous and did not have as many extreme values as the 0–2 cm samples. In order to determine the upper limits of geochemical baseline variation, the deeper sampling depth appears to be more feasible (research objective 6 in Table 5). On the other hand, focusing studies on the topmost layer provides an overview of concentration levels in the most easily accessible part of the soil surface (research objective 6 in Table 5). Studies on the topmost layer could also enable a preliminary assessment of the amount and extent of dust-related, diffuse contamination in urban surface soil. This study illustrated that the organic content does not always explain the elevated concentrations of potentially harmful elements in urban surface soil, but such concentrations are more closely related to the availability of local sources of dusting, creating favourable conditions for site-specific hotspots in urban topsoil.


5 DISCUSSION AND RECOMMENDATIONS

Papers I–VI report that the utilization of geochemical baseline information is important while assessing possible soil contamination and remediation needs. Regional variation due to differences in the geological environment can be high and should be taken into consideration in soil contamination assessment. Various sampling materials may reveal different geochemical baseline levels. The Finnish legislation supports the use of geochemical baseline information and the TAPIR database provides nationally comparable geochemical baseline data that are easily accessed. The recommended leaching methods (HNO₃ and AR) for soil contamination assessment studies that are also used in geochemical baseline studies result in slightly different concentration levels for some elements. The differences in sampling depth do not reveal significant problems for the estimation of proper geochemical baselines. Compared to weak leach, near-total leach is useful when assessing the concentration levels of a possibly contaminated site. However, weak leach (e.g. ammonium acetate leach) provides valuable information for risk assessment purposes, as well as for tracing the origin of elevated concentrations, i.e. whether it is anthropogenic or geogenic.

The broadening of geochemical baseline studies to the urban environment and man-made land areas has provided more exact information on diffuse anthropogenic concentrations. The studies have demonstrated that in Finland, the geochemical baseline level of potentially harmful elements in the urban environment is rather low compared to many other European countries. Some elements, such as lead, tend to enrich in organic matter and may show elevated concentrations in the central parks of cities. This is seen in the city of Helsinki, where the highest concentrations of lead, mercury, arsenic and PCB compounds were found in the organic topsoil (Salla 2010). However, the highest measured lead concentration in Helsinki, 290 mg kg⁻¹ (Ministry of the Environment 2007), is
significantly lower than values reported, for example, in London, UK (>2000 mg Pb kg$^{-1}$) (Appleton et al. 2012a), in Dublin, Ireland (>3000 mg Pb kg$^{-1}$) (Glennon et al. 2014) and in Trondheim, Norway (976 mg Pb kg$^{-1}$) (Ottesen et al. 2008). In addition to the organic matter content, the portion of fine-grained material strongly affects the element concentrations. The highest concentrations are often found in man-made soil material with fine-grained filling dominating (Tarvainen et al. 2013a). It should be noted that in geochemical baseline studies, the samples are usually taken from the topsoil. The chemical quality of artificial landscaping with man-made soil material may, however, vary significantly in depth (Fig. 12). On the other hand, in Norway, topsoil samples were the indicators of the contamination of these artificial landforms (Ottesen et al. 2008). Areas dominated by man-made soil material should always be paid special attention if elevated concentrations are detected. The definition of a geochemical baseline refers to diffuse anthropogenic contamination and not to point-source contamination. Thus, elevated concentrations in man-made soil material may often be considered as representing contamination instead of the geochemical baseline concentration.

5.1 Current use and future applications of geochemical baseline information

At present, information on geochemical baselines is mostly used in soil contamination studies, and the application of geochemical baseline data still needs to find its way to other types of environmental studies. Some land dumping sites (landfills for redundant material) have limits that are based on regional geochemical baseline concentrations. Aggregate production and construction may also utilize the regional geochemical baseline concentrations when located in areas with elevated geochemical baselines.

Geochemical baseline data can be used for identifying and delineating areas that may have environmental or health risks due to naturally occurring elevated concentrations of potentially harmful substances. This type of approach was carried out in the recent ASROCKS project (Guidelines for sustainable exploitation of aggregate resources in areas with elevated arsenic concentrations), in which an area with high arsenic concentrations located in the Tampere-Häme region in southern Finland was delineated partly based on regional geochemical baseline data (corresponds to Southern Pirkanmaa arsenic province, see Fig. 2b) (Lehtinen et al. 2014). The project investigated the potential risks of aggregate production in areas with naturally elevated arsenic concentrations. It also investigated construction sites located in the same area. The main concern was the assessment of pathways and exposure of naturally occurring arsenic related to aggregate production and construction activities.

Geochemical baseline data have also been used for land-use planning purposes. In the municipality of Pirkkala, naturally occurring arsenic anomalies were identified (Tarvainen et al. 2009, 2010, Backman et al. 2010). The known areas with a potential risk for elevated arsenic concentrations are nowadays taken into account in the city
planning and construction in Pirkkala. Site-specific investigations are required if construction is located in an area with elevated arsenic concentrations. It is planned that an arsenic risk map and associated measures will also be included in the building code of the municipality.

New guidelines on the exploitation of excavated land have just been published (Ministry of the Environment 2015). The guidelines designate the classification of excavated land as a waste or exploitative material. In principle, aggregates with elevated background concentrations, i.e. where the concentration is higher than the threshold value given in the Government Decree (214/2007), are not considered contaminated. They can be exploited or placed in areas with similar or higher regional geochemical baseline concentrations. The regional geochemical baseline is also taken into consideration when evaluating the suitability of excavated land for specific landfill sites. The guidelines state that without any site-specific environmental permit, the landfill sites located on important groundwater areas may not accept material with concentrations over the threshold value or regional geochemical baseline. In the Tampere region, the regional baseline has already been used as a screening value for some landfill sites (T. Tarvainen, personal communication, February 2015).

5.2 TAPIR – Finnish national geochemical baseline database

The TAPIR database has been recognized as a data source that provides scientifically sound geochemical baseline values that can be used at the national level for transparent decision-making. The database is regularly updated and more precise information on regional or local geochemical baselines is provided when sufficient data are available. This will expand the use of geochemical baseline information from soil contamination studies, for example, to delineate potential risk areas, for risk assessment procedures as well as for environmental baseline studies (Fig. 13) (Jarva & Tarvainen 2014).

While the TAPIR database is meant to distribute scientifically sound statistical information on geochemical baselines, certain restrictions and guidelines are given for data providers. For inorganic substances, the database only accepts analysis results from the <2 mm particle-size fraction. The leaching method has to be either aqua regia extraction or concentrated nitric acid leach, as these are the suggested methods for soil contamination assessment (Ministry of the Environment 2007, 2014a). Samples are preferred to be taken from the upper part of the ground, i.e. from topsoil. Single samples are favoured, but composite samples are also accepted in the database. The TAPIR database also gathers information on baseline concentrations of organic compounds, mainly PAH and PCB compounds. The concentrations can be reported as total concentrations of PAH compounds or PCB congeners based on Appendix 1 of the Government Decree (214/2007), or as concentrations of a single compound or congener. The analysis methods for organic compounds should follow the ones recommended for soil contamination assessment (Ministry of the Environment 2007, 2014a). As described in Paper IV, acceptable concentration levels for each element to be considered as a baseline concentration have been determined. The lower guideline value is set as the maximum acceptable concentration for those trace elements and organic compounds that are indicated in the Decree (214/2007). For other elements, the limits are based on other existing risk-based reference values. However, GTK as a managing authority of the TAPIR database is able to decide whether higher concentrations are also eligible to be included in the database, e.g. due to the specific geological conditions of an area.

While existing data on geochemical baselines based on aqua regia extraction or concentrated nitric acid leach from the <2 mm particle-size fraction is still rare, the TAPIR database also contains geochemical data that are derived from the <0.06 mm particle-size fraction. The primary dataset within the TAPIR database is derived from regional geochemical mapping in Finland, where samples represent glacial till and have been taken as composite samples from an average depth of 1.5 m. The samples are analysed with aqua regia extraction from the <0.06 mm fraction (Salminen 1995). Tarvainen (1995) has defined linear functional relationships that can be used to estimate element concentrations in
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the coarse till fraction (<2 mm) if concentrations in the fine fraction (<0.06 mm) have been determined. These linear functions have been used in the TAPIR database for Co, Cr, Cu, Ni, V and Zn to calculate concentrations that correspond to the <2mm particle-size fraction.

Currently, it is possible to interactively calculate geochemical baseline statistics, including the upper limit of baseline variation, for a site of interest, and statistics are not only provided for pre-described geochemical provinces, as previously. A circle with a radius from 2 to 50 kilometres can be drawn and geochemical baseline statistics for different soil parent materials and provinces are provided by the database for elements that have 30 analysis results at minimum (Figs. 14 and 15) (Jarva & Tarvainen 2014). This update enables more effective use of geochemical baseline information in various environmental studies.

The TAPIR database provides information on inorganic elements prescribed in the Appendix 1 of the soil contamination-related Government Decree (214/2007), as well as some other elements (e.g. thallium, beryllium, molybdenum, tin) considered to be significant due to their environmental or health impacts. It is, however, the spirit of the law (Government Decree 214/2007) that soil contamination studies should be based on all relevant harmful elements and substances in question, not only on elements that are prescribed in the Appendix of the Government Decree (214/2007). This lays down the necessity to update the TAPIR database with elements that will appear in soil contamination studies. For example, the lack of information on geochemical background concentrations of elements appearing in shooting ranges (e.g. bismuth, tungsten) and platinum-group metals (e.g. palladium, platinum, rhodium) has been acknowledged. The replacement of lead with steel, bismuth, tungsten, tin and zinc in bullets and shot (Kajander & Parri 2014) has resulted in elevated concentrations of these elements in soil deposits (Tarvainen et al. 2011c). Traffic-related platinum group elements in urban surface soils have been studied and elevated concentrations are strongly related to surface soils adjacent to major roads with high traffic volumes (e.g. Morton et al. 2001, Morcelli et al. 2005, Tarvainen & Jarva 2009a, Mihaljević et al. 2013).

Several regional geochemical anomalies exist in Finland with clearly elevated concentrations of potentially harmful elements that are geological

Fig. 13. A screen shot of the TAPIR database starting page. The database is available in Finnish and in English. Source: http://gtkdata.gtk.fi/tapir/
Fig. 14. A screen shot of the TAPIR database after selecting a 15 km radius circle around the area of interest (black dot). Existing sampling points can be seen on the screen. Orange circles denote till and green circles sand. Triangles denote humus. By clicking on the calculator button, statistics for selected soil parent material from the selected area (blue circle) will appear in a separate window. Source: http://gtkdata.gtk.fi/tapir/index.html

Fig. 15. A screen shot of the TAPIR database after selecting a 15 km radius circle around the area of interest (black dot) and selecting samples existing within the geochemical province (blue figure). Existing sampling points can be seen on the screen. Orange circles denote till and green circle sand. Triangles denote humus. By clicking on the calculator button, statistics for selected soil parent materials from the selected area (blue figure) will appear in a separate window. Source: http://gtkdata.gtk.fi/tapir/index.html
in origin. The most well known is the Tampere–Häme region, with elevated concentrations of arsenic in bedrock, soil parent material and groundwater. This area is also recognized in the TAPIR database as a separate geochemical province, the Southern Pirkanmaa arsenic province (Fig. 2b). Elevated concentrations in soil deposits can also be related to high mineralisation. This is true, for example, in the Kittilä area (Fig. 2b), which is recognized in the TAPIR database with elevated concentrations of arsenic, cobalt, chromium, nickel and vanadium, and is also indicated as a metallogenic area with precious metals (mainly gold) (GTK 2012, Peltoniemi-Taivalkoski et al. 2013).

5.3 The use of geochemical baseline information in risk assessment studies

In the preliminary risk assessment of soil contamination, the source, pathway and recipient are recognized. The risk may be directed to the environment, human health or living organisms. The risk assessment process in soil contamination studies has been divided into three parts: risk identification, risk quantification and risk characterization. If the final analysis reveals that the risk is acceptable for the current state, remediation is not needed. However, this does not necessarily mean that no risk exists. Monitoring results or land use change may lead to the need for remediation (Ministry of the Environment 2014a). Although risk–based soil contamination assessment has been the key policy principle in Finland since 2007, risk–based remediation is still rare. According to Reinikainen (2014), up to 95% of the remediation cases between 2007 and 2013 were based on guideline values instead of site–specific risk assessment. The updated national guidelines further encourage risk–based assessment, while sustainable risk management is given stronger weighting (Ministry of the Environment 2014a).

Feasibility studies are commonly used to investigate preferable and applicable remedial measures. Rosén (2010) described five major steps of feasibility studies that were identified from Sweden and Denmark: 1) setting the remediation goal, 2) identifying applicable remedial measures, 3) evaluating applicable remedial methods, 4) identifying the criteria for the evaluation of applicable remedial methods, including cost–benefit and effective analysis, and 5) selecting the best option and also evaluating this from social and practical perspectives. In both countries, the remediation goals can be set by reducing the contamination source, by leaving contaminants in the ground fully or partly based on protective measures, or by administrative measures. In Sweden, the first option is the most common, while protective measures are more often applied in Denmark. Both countries use site–specific risk assessment for setting remediation goals, although with a different approach and emphasis (Rosén 2010).

In Norway, risk–based soil contamination assessment has taken place since the early 1990s, when the Norwegian Pollution Control Authority (Statens forurensningstilsyn, SFT) published technical guidelines for environmental site investigations (Statens forurensningstilsyn 1991, Norwegian Pollution Control Authority 1999). In principle, in cases where the soil contamination may pose a risk, the land must be remediated to a state in which it is suitable for use. In many cases, the present land use does not pose a serious danger to human health or the environment, and remediation has not therefore been carried out. However, these sites are followed up, because a land use change could lead to health risks or the leakage of hazardous substances (Norwegian Environment Agency 2016).

In Sweden, the potential risk due to soil contamination is assessed from different perspectives based on four main components: hazard assessment, contamination level, migration potential and protection value. In simplified risk assessments, contaminant concentrations measured on site are compared with generic or site–specific guideline values. While assessing the potential risks associated with the contamination level, guideline values exist for contaminated soil against which the studied concentrations are compared. In addition, the deviation from the reference value, i.e. geochemical background level, is calculated. Finally, the concentration of contaminants and volume of contaminated material are determined. All factors are then studied together in order to provide an assessment of the contamination level for

The bioavailability of potentially harmful elements plays a major role in risk assessment processes for potentially contaminated soils. The use of geochemical baselines as screening or reference values for soil contamination assessment may pose certain challenges. For example, Lax & Andersson (2011) highlighted a problem that may occur if anthropogenic pollution is undetected in areas where natural background concentration levels are high. The mobility of certain elements or substances may be higher from anthropogenic sources than from naturally occurring forms. If speciation or mobility is not studied, potential exposure and related risks may remain unnoticed. In the UK, lead bioaccessibility from urban topsoils and mineralisation has been investigated (Appleton et al. 2012a, Appleton et al. 2013, Palmer et al. 2015). It was argued that the origin and mineralogy of soil deposits can impact on the bioaccessibility, and some anthropogenic pollution sources are potentially more soluble in the environment and thus are more bioavailable (Appleton et al. 2012b, Palmer et al. 2015). Similar findings were identified in Paper III, where the leachability of metal-contaminated soil was compared to the geochemical baseline concentration in the course of chemical characterization. The solubility of potentially harmful elements of geogenic origin has further been studied by Tarvainen & Jarva (2009b) with the determination of the distribution coefficient, i.e. the $K_d$ value. It was found that in most cases the $K_d$ value was high if elements were geogenic in origin. In areas with an anthropogenic load, the $K_d$ values varied greatly. The $K_d$ value was used to determine the highest acceptable concentration in soil deposits without any risk for groundwater pollution. In some cases, the guideline value was not considered to be enough to protect groundwater. Thus, site-specific investigations were suggested in the case of soil contamination in close vicinity to vulnerable aquifers (Tarvainen et al. 2011a,b,c). Palmer et al. (2015) also questioned whether diffuse anthropogenic input is considered as a baseline if an element has a non-threshold toxicity character. This is true, for example, for lead. Here, it must be noted that in Finland the guideline values describe maximum acceptable risks to the environment and human health. Only the guideline values that are based on ecological risks can be modified based on regional geochemical baseline concentrations, as explained in Paper IV.

In Finland, acid sulphate soils are specific phenomena that are particularly found in the areas below the highest water level of the ancient Littorina Sea (Edén et al. 2012). As a result of oxidation, the pH of these sulphur layers decreases, which in turn induces the solubility of harmful metals from the sediments. Studies have shown that the total contents of potentially harmful elements in sulphidic sediments are not higher than in non-sulphidic clays from adjacent areas, but the mobilisation may be higher from acid sulphate sediments (Sohlenius & Öborn 2004, Fältmarsch et al. 2008 and references therein). In urban development, the potential mobility of metals from acid sulphate sediments should be carefully taken into account in the earth construction of these areas, as when the sediments are excavated they will become oxidized. Even if the total concentrations of metals are low, their mobilisation may significantly increase when oxidized and thus pose a risk to the environment (Tarvainen & Eklund 2013).

6 CONCLUSIONS

The studies of this thesis have introduced applicable investigation methods for geochemical baseline studies. They have provided information on the interpretation and application of geochemical baseline information for different purposes. The results of the presented research topics are already utilized in international geochemical projects dealing with baseline studies when applicable. Natural variation in geochemical baseline concentrations is significant in Finland. Threshold values given by the Government Decree (214/2007) are occasionally exceeded, but regional differences in geochemical baseline concentrations are high. Urban areas differ in their geological characteristics, land use and potential environmental load, and separate baseline studies are thus needed for each major urban region.
However, even in urban soils, the natural background can be more dominant than the anthropogenic diffuse input.

Various national environmental applications could benefit from the information on regional geochemical baseline concentrations. A national geochemical baseline database, TAPIR, is already widely used among environmental authorities, land use planners and consultant companies dealing with environmental issues. Information on geochemical baseline concentrations can be used for different environmental assessment purposes, such as in the definition of the baseline status, and they also provide background information for land use planning. At present, geochemical baselines are mostly utilized in soil contamination studies. Reliable data on the geochemical baselines is of special importance in regions where the geochemical baselines may exceed the threshold values given in the Government Decree (214/2007). Such data may be utilised while locating the activities in areas with elevated geochemical baseline concentrations. Reliable information also enables case-specific guidelines for soil contamination assessment to be determined. The recalculations of regional guideline values give tools to better assess the remediation needs as well as to choose the best available remediation technique for the area in question. On the other hand, it may even prevent unnecessary remediation. The latest applications are related to the baseline reports of the operators in question in accordance with the Environmental Protection Act (527/2014), as well as to the exploitation of excavated land in accordance with the Environmental Protection Act (527/2014) and Waste Act (646/2011). Thus, the applications of geochemical baseline information are manifold, ranging from geological and environmental applications to the protection of human health and finally to sustainable and cost-effective administrative decisions.

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Ministry of the Environment 2014b. Ympäristönsuojelu- lakulain mukainen perustuselaysys – Ohje toiminnan-


**List of regulations:**
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- Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007)
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This PhD thesis is comprised of a synopsis and six original articles dealing with different applications and uses of geochemical baselines in soil contamination assessment and other environmental decision processes. The synopsis provides an overview of the development of guidelines and legislation related to soil contamination in Finland, with the main focus on geochemical baselines.

The growing demand to increase sustainable land management in urban areas has involved various applications of geochemical surveys. The thesis focuses on practical applications and further recommendations for geochemical baselines based on literature reviews, interpretation of the statistical analysis of geochemical baseline data and scientific discussions. The utilization of geochemical baseline information is important when assessing possible soil contamination and remediation needs. Regional variation due to differences in the geological environment can be high and should be taken into consideration in contamination assessment. Various sampling materials may reveal different geochemical baseline levels. This thesis shows how geochemical baselines in the assessment of soil contamination in Finland are outlined, with suggestions for further applications in multidisciplinary studies and recommendations for future research needs.