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SURGE Project

Geochemical baseline for heavy metals and organic pollutants in topsoils in the greater Dublin area

Technical Report

Geological Survey of Ireland

Dublin SURGE Project

Geochemical baseline for heavy metals and organic pollutants in topsoils in the greater Dublin area

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Geological Survey of Ireland

The Geological Survey of Ireland founded in 1845, is the National Earth Science Agency. It is responsible for providing geological advice and information, and for the acquisition of data for this purpose. GSI produces a range of products including maps, reports and databases and acts as a knowledge centre and project partner in all aspects of Irish geology. GSI is a division of the Department of Communications, Energy & Natural Resources (DCENR).

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Dublin SURGE Project

The Dublin SURGE Project sets out to complete a baseline survey of heavy metals and organic chemicals in topsoils in the greater Dublin area. As a result of human activities in the urban environment, concentrations of chemicals in urban soils often reach levels that may give rise to concern for human health. The project will provide information on soil chemistry in the urban environment relevant to the protection of human health, compliance with environmental legislation, land-use planning and urban regeneration.

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Disclaimer

The soil geochemical data presented in this report are from individual sites, which were sampled as part of a baseline geochemical survey. The results should only be used to set a regional context, not as the basis for interpretations concerning specific sites. Interpretations relating to specific sites should be based on follow-up site-specific investigations.

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Foreword

Soil is a wonderful and valuable natural resource on a par with water, air and sunlight in terms of our survival on planet earth.

Irish soils were formed over long timescales by weathering and glacial processes acting on the underlying bedrock. This bedrock shows great diversity – limestone, granite, shale, sandstone etc. across Ireland – and the derived soils reflect this variability in their mineralogical and chemical composition. Such natural soils, full of beneficial nutrients and trace elements, are the basis of our booming agricultural success which provides such economic benefit to our country.

However, in our cities and urban areas soil quality has often been compromised to a greater or lesser extent by human activity. The extent to which urban soils in Ireland have been compromised is not known with any certainty. The levels of heavy metals and organic compounds in our soils have not so far been addressed in any systematic way. It is important to determine the levels of these potentially harmful elements and chemical compounds in the context of human health protection, better land use planning and soil remediation strategies.

The present study sets out to determine the geochemical *baseline* for topsoils in the greater Dublin area. Such a baseline provides a snapshot today of the chemical status of Dublin soil against which future change can be measured. Urban soil is a complex mixture of natural soil (derived from geogenic sources) and man-made (anthropogenic) contributions (often over centuries) from waste materials, landfill, emissions, airborne deposition etc. In a city like Dublin with more than 1000 years of growth and development we might expect to see this legacy of historic industrial and human activity reflected in its soils and indeed we do see just that.

The maps and data presented in our study show that the soils of central Dublin have been impacted most with elevated levels of potentially harmful elements such as arsenic, lead, mercury, copper, zinc and organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). There is an outward gradation to less-impacted suburban soils.

The Dublin data may be used to inform the setting of Soil Guideline Values (SGV's) for our urban areas, in future landuse planning and to highlight areas where potentially harmful elements and persistent organic pollutants are elevated and where remedial actions may be needed from an environmental and public health perspective. Finally it is recommended that this study will act as the impetus to establish an Inter-Agency technical advisory group to drive a co-ordinated approach to soil quality in urban areas in Ireland.

Pat O'Connor
Acting Director (Retired), Geological Survey of Ireland
March 2012

Executive Summary

The Dublin SURGE (Soil Urban Geochemistry) Project aims to create a baseline dataset of heavy metals and persistent organic pollutants (POPs) in Dublin topsoils for the first time. Most cities have well-established monitoring systems for the environmental quality of air and water, while soils as an environmental medium have received comparatively little attention. In urban areas, human activities over time can alter soil's natural chemical and physical properties through the addition of chemical contaminants, waste matter and the disturbance of soil through excavation and landscaping. This project provides information on soil chemistry in the urban environment relevant to the protection of human health, compliance with environmental legislation, land-use planning and urban regeneration.

A total of 1058 samples were taken in topsoil (0-10cm depth) in the greater Dublin area in October and November 2009. Sample locations were chosen randomly to give an overview of baseline conditions in the city. All samples were analysed for 31 inorganic elements including heavy metals.

Results for heavy metals indicate that the concentrations of lead, copper, zinc and mercury are strongly influenced by human activities. The concentrations of these metals are elevated in the docklands, inner city and heavy industry areas. Sources of heavy metals in these areas include historic industry such as metal and chemical works, coal burning in homes and industry, reuse of contaminated soil and modern traffic. Lead concentrations are considered high in inner city locations, a trend which can be attributed to the historic use of leaded paint and petrol in addition to the sources described above.

Concentrations of other inorganic elements in topsoil in the greater Dublin area show patterns which are strongly related to regional bedrock parent material (limestones in the Dublin basin region and the Leinster granites in southern Co. Dublin).

Of the 1058 samples taken, a subset of 194 samples were also analysed for the following persistent organic pollutants:

- Polycyclic aromatic hydrocarbons (PAHs) and
- Polychlorinated bipheyls (PCBs).

Persistent organic pollutants are chemicals which do not readily break down in soil, air or water and they can be taken up by plants, animals and humans through the food chain. Therefore they are a cause of concern for human health and the environment. PAHs are sourced mainly from human activities, namely the combustion of organic matter and fossil fuels in domestic fires, industry and vehicle engines. PAHs are known to cause adverse human health effects such as dermatitis and bronchitis and they are classed as potential human carcinogens. PCBs are man-made chemicals which were synthesised from the 1930s to the 1980s for use in electrical equipment and building materials. PCBs are classed as potential human carcinogens and potential human endocrine disruptors (affecting the reproductive and hormonal systems). Humans can be exposed to PAHs and PCBs in soil by gardening or playing

in contaminated soil, eating food grown in contaminated soil or by inhaling contaminated soil dust which is brought into the home on the wind or on shoes or clothes.

PAHs were detected across the city, with maximum concentrations occurring in the city centre. Concentrations decline towards the outer suburbs. This trend reflects historical sources of domestic coal burning, industrial emissions and modern traffic which are associated with city centre locations. PAH compositions indicated that most PAHs in soils may be attributed to historical coal combustion. Other potential sources of PAH concentrations in Dublin soils include contaminated fill materials in reclaimed land, bonfires, creosote treated wood and recycled tyre products.

Results for PCBs in soil indicate isolated, low level detections of PCBs in Dublin, mainly in the city centre. The PCB compositions in soils indicate that contamination is probably associated with historical industrial sources and old paint rather than modern, active sources.

Advances in environmental protection have been made in recent decades in Dublin with the bituminous coal burning ban, the regulation and licensing of industry and remediation of many inner city contaminated sites through redevelopment. Although traffic volumes have increased over the years and vehicle emissions are now the main pressure on Dublin’s air quality, vehicle engines are becoming cleaner. These factors are reducing heavy metal and PAHs emissions which can impact on topsoil quality. However active measures are required to ensure good land management practices in relation to the reuse of contaminated soil and dealing with contaminated soils.

Ireland does not yet have dedicated contaminated land guidance to help landowners assess the potential risks from contaminated land to human health and the environment. Other countries have successfully established guidance and regulation through collaboration of environmental experts, health authorities and regulators. It is recommended that a contaminated land guidance and regulatory regime is put in place for Ireland, in order to prevent deterioration of Ireland’s soil resource, especially in public areas where people can come into contact with urban soil.

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1 Introduction

Soil is an essential component of terrestrial ecosystems which fulfills numerous important functions, such as acting as a growing medium for plants, filtering and storing water, supporting biodiversity, nutrient cycling and acting as a foundation for built structures (Bullock and Gregory, 1991). In urban areas, human activities over time can alter soil's natural chemical and physical properties through the addition of organic and inorganic material, waste matter and the disturbance of soil through excavation and landscaping. This may lead to soil contamination.

Concentrations of contaminants in urban soils may reach levels that give rise to concern for human health. These are of particular concern in sensitive public land uses where human contact with soil is likely, such as in schools, playgrounds, parks and vegetable gardens, especially since 80% of the European population now lives in cities. In 2011, 62% of the Irish population lived in urban areas and the trend towards urbaisation is increasing (CSO, 2012) Most cities have well-established monitoring systems for air and water, while soils have received comparatively little attention. Sources of contaminants in soils include point sources (e.g. spillage and leakage) and diffuse sources such as deposition from atmospheric contamination.

According to the EPA's 4th 'State of the Environment' report (EPA, 2008), one of the key challenges to Ireland's environment is to reverse the degradation of the water environment, flora and fauna and the soil environment. In relation to the soil environment, the report identified the need to identify, remediate and manage contaminated land sites and to develop legislation aimed at dealing with contaminated land. Soil is a natural resource which forms over long periods of time and so it is vital to prevent its degradation. In order to prevent further degradation of soils, in particular urban soils, soil needs to be afforded the same protection as is given to air and water in Ireland. Unlike many other EU Member States, Ireland lacks a dedicated regulatory regime for managing soil resources and contaminated land. Existing domestic legislation deals indirectly with the prevention and remediation of contaminated land where for instance, land affects other environmental media, such as air or water, where development is planned or where the land comes under the waste management or industrial licensing regimes.

The need for concerted soil protection in Europe was highlighted in 2006 when the European Commission adopted the Thematic Strategy for Soil Protection (Commission of the EC, 2006a). The strategy included a proposal for a Soil Framework Directive which aims to ensure the sustainable use of soil through measures including pollution prevention and the implementation of national inventories, monitoring programmes and remediation strategies for contaminated sites in EU Member States. The proposal is currently under consideration by European institutions.

The Geological Surveys of Europe (EuroGeoSurveys) have initiated an urban soils project, known as the URGE (urban geochemistry) project, in order to highlight the importance of urban soils to environmental health in European cities. Under this initiative, the Geological Survey of Ireland, in partnership with the Geological Survey of Norway (NGU), undertook systematic geochemical mapping of persistent organic pollutants and heavy metals in soils in the greater Dublin urban area, known as the Dublin SURGE Project.

The project commenced with a city-wide soil sampling programme in October and November 2009. The study area covers public lands in all of the Dublin City Council area and parts of Fingal, South Dublin and Dún Laoghaire-Rathdown County Council areas.

This report describes results for inorganic elements and persistent organic pollutants in Dublin's topsoil. Soil was tested for inorganic elements which include thirty heavy metals and metalloids. These encompass the major elements and trace elements found in soils:

- Aluminium (Al)
- Arsenic (As)
- Barium (Ba)
- Beryllium (Be)
- Boron (B)
- Cadmium (Cd)
- Calcium (Ca)
- Cerium (Ce)
- Chromium (Cr)
- Cobalt (Co)
- Copper (Cu)
- Iron (Fe)
- Lanthanum (La)
- Lead (Pb)
- Lithium (Li)
- Magnesium (Mg)
- Manganese (Mn)
- Mercury (Hg)
- Molybdenum (Mo)
- Nickel (Ni)
- Potassium (K)
- Scandium (Sc)
- Silicon (Si)
- Sodium (Na)
- Strontium (Sr)
- Titanium (Ti)
- Vanadium (V)
- Yttrium (Y)
- Zinc (Zn) and
- Zirconium (Zr).

One non-metal was also tested, Phosphorus (P).

Soil was tested for persistent organic pollutants including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

The objectives of the project are to:

- **Create a baseline dataset of soil geochemistry in Dublin.** A systematically produced baseline will provide a geochemical reference that may be used for purposes such as soil monitoring and contaminated site assessment in the greater Dublin area. The baseline level is the concentration at a specific point in time of a chemical element, species or compound in a sample of geological material (FOREGS definition cited in Johnson and Ander, 2008).

  The baseline accounts for both natural and anthropogenic concentrations. In the case of organic contaminants, all PCBs concentrations and the vast majority of PAH concentrations in soils are attributed to anthropogenic rather than natural sources. Background levels are those which are considered to be naturally occurring in geological materials - these are more significant for inorganic elements.

The importance of understanding present environmental conditions can be crucial in responding to major soil contamination events resulting from catastrophes such as flooding in New Orleans (2005), the Buncefield oil refinery fire in the U.K. (2005) and the Chernobyl nuclear accident (1986) (Johnson and Ander, 2008). Baselines are also an integral part of the risk assessment process for contaminated soils, where knowing “normal” soil conditions is fundamental to establishing health criteria above which there may be a risk to human health or the environment (Section 4.3).

- **Assess the extent and nature of metals and organic chemicals in Dublin soils, both natural and man-made.** Due to the importation of soil for land reclamation, landscaping and construction, the soils of Dublin city are highly variable in character. Reworked natural soils and artificial soils containing various waste materials commonly occur alongside natural, in-situ soils in the city’s urban fabric. For the first time, an understanding will be gained of the geochemistry of both natural and man-made soils in Dublin city.

- **Develop geochemical maps of Dublin soils that can be used for land use planning, environmental management and health risk assessment.** It is envisaged that the Dublin SURGE data will allow local, environmental and health authorities to take soil geochemistry into account as an important consideration in protecting the environment and human health from soil contamination. The data may be used to help identify areas possibly in need of remediation, to contribute to more informed brownfield and suburban development and to facilitate the shift towards considering soil as an important resource in the wider environment.

2 Study area

Dublin is the Ireland's capital and largest city, with a population of 1.2 million people (CSO, 2010). It is located on Ireland's east coast and has a large urban footprint of over 430km^2 (CDM, 2009). This study covers the greater Dublin area including Dublin's satellite towns, covering an area of just over 500km^2. The study area location and extent are indicated in Figure 1. The area encompasses all of the Dublin City Council administrative area and parts of South Dublin, Dún Laoghaire-Rathdown and Fingal County Council administrative areas. The following sections describe the geological setting and the land use history of the greater Dublin area.

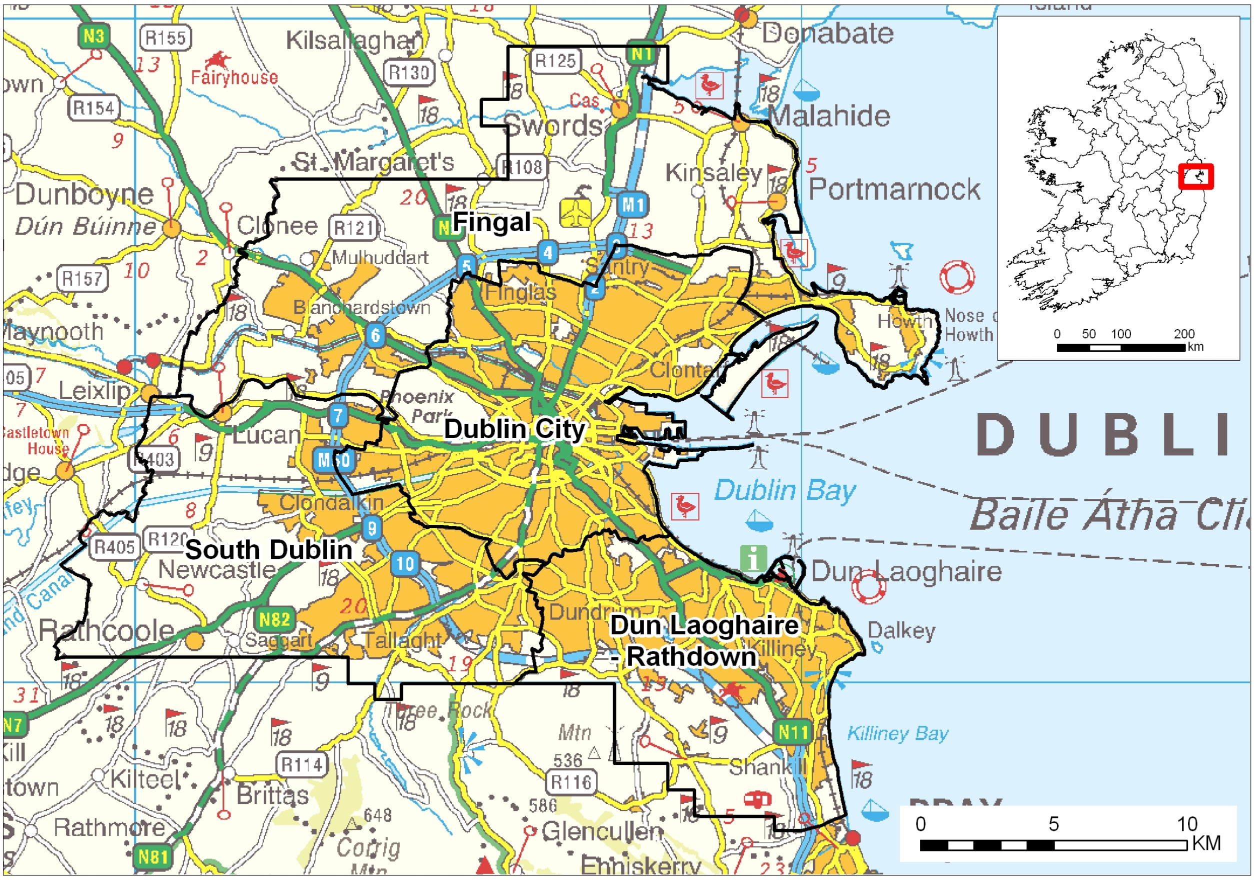


Figure 1 Study area showing local authority administrative areas

2.1 Geology and soils

The bedrock and subsoil geology of Dublin city is shown in Figure 2. Dublin city is underlain by the Dublin Basin, a geological region composed of poorly differentiated Lower Carboniferous basinal limestones and shale, known colloquially as Calp (McConnell, 1994). Calp units typically consist of dark grey, fine grained, argillaceous (muddy) limestone interbedded with black shales.

Dublin Bay is confined by the granite headland of Dalkey to the south and the quartzite peninsula of Howth in the north (McConnell, 1994). The city is bounded in the south by the upland Leinster granite region of the Wicklow mountains. The Leinster granites are surrounded by a metamorphosed region of fine grained metasediments (schists, shales and siltstones) known as the Ribband Group (McConnell, 1994). The Ribband Group hosts a variety of mineral deposits including lithium, tungsten, lead and zinc (McArdle *et al.* 1989). The eastern margin of the Leinster Granites has significant lead and zinc-bearing veins composed of galena, sphalerite and pyrite (McArdle *et al.* 1989). Economic mining in this area included the extraction of Pb, Cu, Fe, S and Ag at Ballycorus and Killiney (McConnell, 1994).

In the greater Dublin area, there are extensive glacial sediments overlying bedrock, consisting of widespread boulder clay or till of varying thicknesses (up to 40m) and areas of thick alluvial material along the River Liffey. Subsoil composition is dominated by the parent lithology, with tills mainly derived from limestone in central and northern Dublin city, and tills derived from granites in the south.

Topsoil is the fertile, uppermost layer of soil which is usually up to 20cm deep. Natural topsoils in the greater Dublin area are classed as grey brown podzolics (calcareous soils formed from limestone parent material) (Fay *et al.,* 2007).However, much of the soil in Dublin's inner city has been subject to human alteration through land reclamation and construction, and is therefore known as "made ground". Made ground is a deposit consisting of a mixture of natural soil and anthropogenic (man-made) materials and is typically used to reclaim land by filling marshes and low-lying ground. Made ground is characterised by a high degree of variation in constituents, which often include plastic, brick, glass, ceramics, construction rubble and historical industrial waste such as clinker and metals. Areas of made ground in the city are mapped on the subsoil map (Figure 2), most notably in the docklands and quays areas. 1.7% of the study area is covered with made ground. Between 3 and 6m of fill was required to bring Dublin's intertidal zone above the high tide level to the region of 3.4m O.D (Farrell and Wall, 1990). Dublin's oldest area around Christchurch is underlain by up to 4m of made ground of archaeological significance (Farrell and Wall, 1990). Ash and clinker from the power generation and coal burning industries are known to have been used historically as fill in the docklands, port and low lying inner city coastal areas.

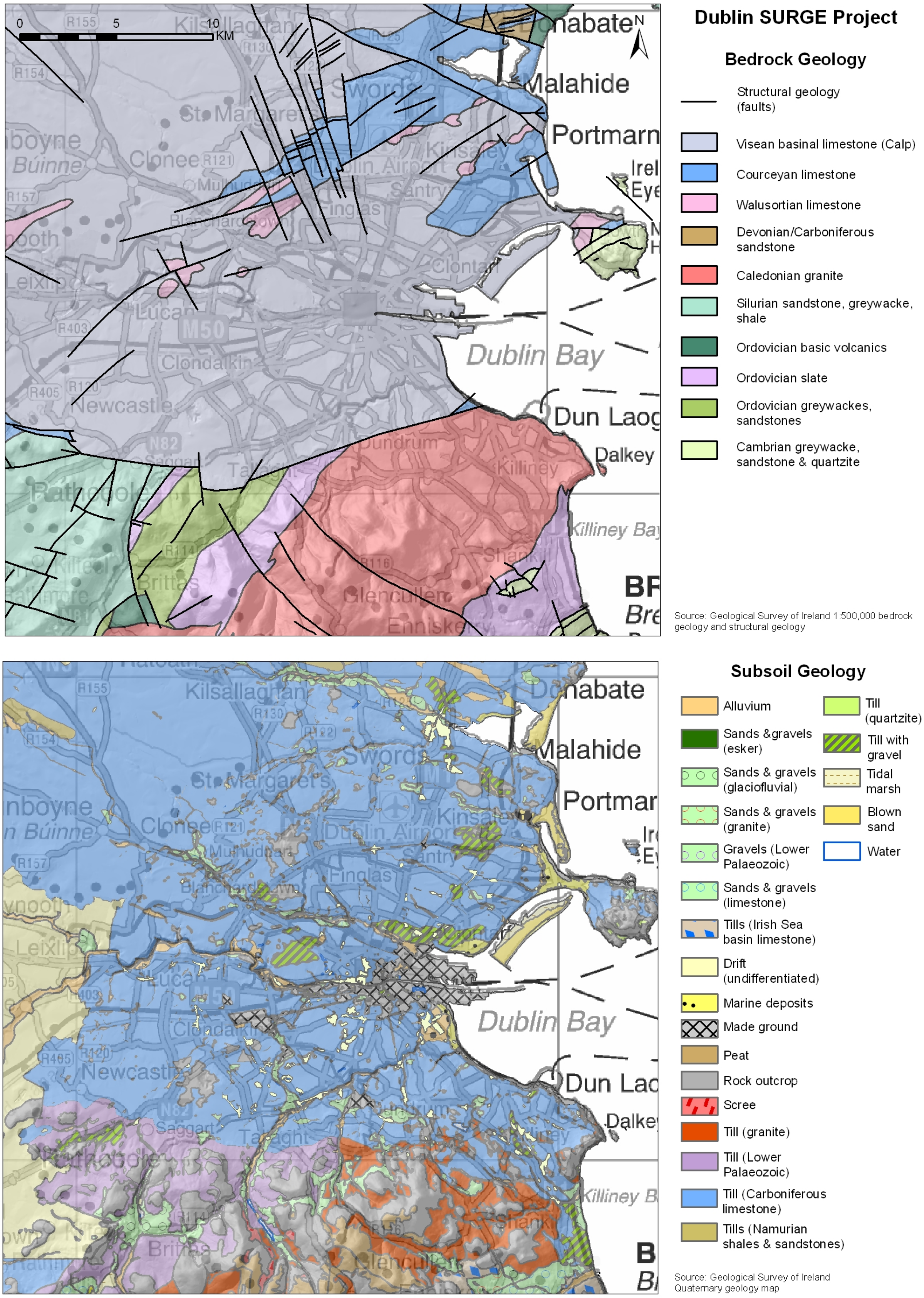
2.2 Existing soil geochemical information

At present, no systematic baseline geochemical information exists for Irish urban environments. The geochemistry of rural Irish topsoils has been mapped as part of the Soil Geochemical Atlas of Ireland (Fay *et al*., 2007) and the FOREGS Geochemical Atlas of Europe (Salminen, 2005). The FOREGS Atlas mapped the geochemistry of Europe using 1588 samples of various environmental media from 26 countries at a resolution of one sample per 4700km^2. As part of soil sampling, 11 topsoil samples (2-25cm depth) were taken in Ireland and were analysed for a range of 56 inorganic elements. Results showed that the distribution of heavy metals is influenced by regional geology and areas of industry and intensive agriculture.

Baseline concentrations of 40 inorganic elements were determined for rural soils in Ireland as part of the Soil Geochemical Atlas of Ireland which was completed by Teagasc and the EPA from 1995 to 2006 (Fay *et al*., 2007). The project took 1310 soil samples on the basis of 2 samples per 10km x 10km square on the National Grid. The soil samples constitute the National Soil Database (NSDB). The study found that baseline topsoil concentrations correlated closely with underlying regional geology. Some localised elevated concentrations of elements were identified in relation to urban areas, mining and agricultural activities. Eight samples were taken in rural areas in the greater Dublin area and these were reanalysed with Dublin SURGE samples. This exercise was undertaken to create a tie-in point between the two surveys. NSDB samples analysed using the SURGE methodologies are used as a rural baseline which is directly comparable to the urban SURGE baseline. Reference is made to the retested NSDB concentrations when discussing individual inorganic element results.

A study completed in 1995 (McGrath, 1995) determined organic pollutant (PCBs and organochlorine pesticides) and trace element concentrations in topsoil in a small number of agricultural, urban and industrial soils in Ireland. Twenty-two soil samples (0-10cm depth) were taken in twelve counties around Ireland. The study concluded that the PCB levels observed in rural and urban areas constituted trace background levels, and that the higher level observed in an industrial area was due to the presence of industry there for the previous 30 years. The same study measured heavy metals Cd, Cu, Cr, Hg, Ni, Pb and Zn and detected the highest levels of these in urban gardens. Pb was notably elevated in urban gardens and this was attributed to atmospheric deposition of Pb in urban areas.

A number of studies carried out by NUI Galway determined heavy metal concentrations in topsoils in public open space in Galway city. Zhang (2005) took 166 soil samples (0-10cm) throughout the city and determined that there were anthropogenic enrichments of the heavy metals Cu, Pb, Zn and As in the city centre area. Sources were attributed to traffic, unregulated dumping, bonfires and herbicide application in parks. Localised areas of heavy metal contamination due to bonfires and unregulated dumping of hospital and industrial waste in three public open spaces in Galway were identified by Dao *et. al.* (2010a and 2010b) and Carr e*t. al.* (2008).



Source: Geological Survey of Ireland 1:500,000 bedrock geology and structural geology

Source: Geological Survey of Ireland Quaternary geology map

Figure 2 Bedrock and subsoil geology maps for the greater Dublin area

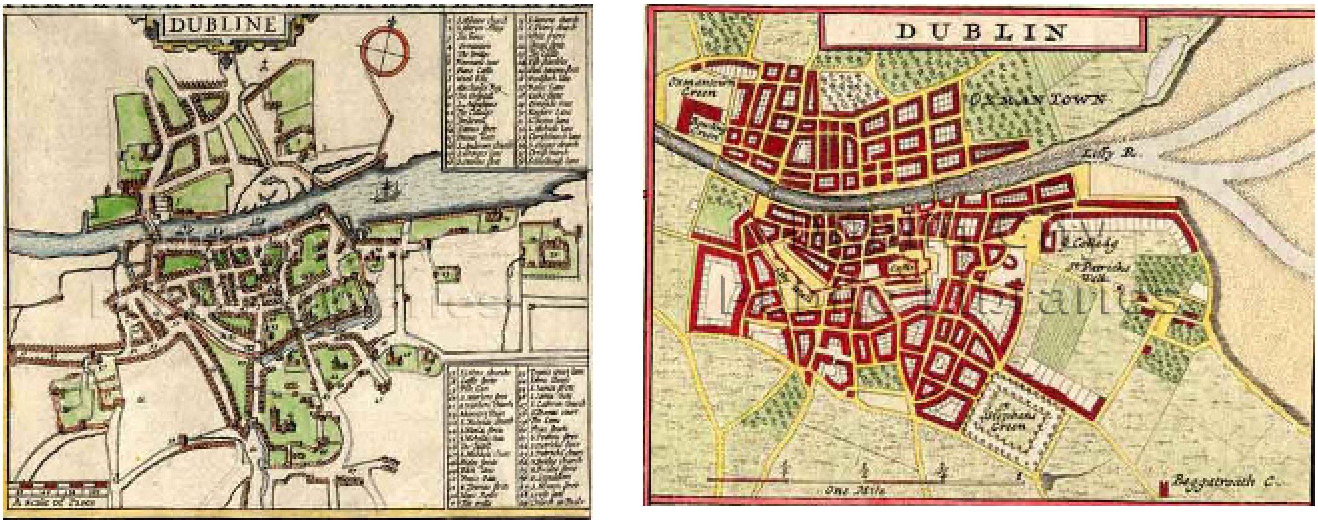
2.3 Land use and industry in the greater Dublin area

2.3.1 History of Dublin's growth and industrial development

Dublin was founded in the 9th century at Wood Quay, an area on the south bank of the River Liffey in the modern city centre. By medieval times, a process of land reclamation was underway to allow for the development of port facilities and further city development along the Liffey and east into Dublin Bay's intertidal zone. Land reclamation activities included the building of quay walls and the filling of marshy land. Through the 17th and 18th centuries, large areas to the east of the town were reclaimed, providing areas for settlement at Clontarf and Ringsend.

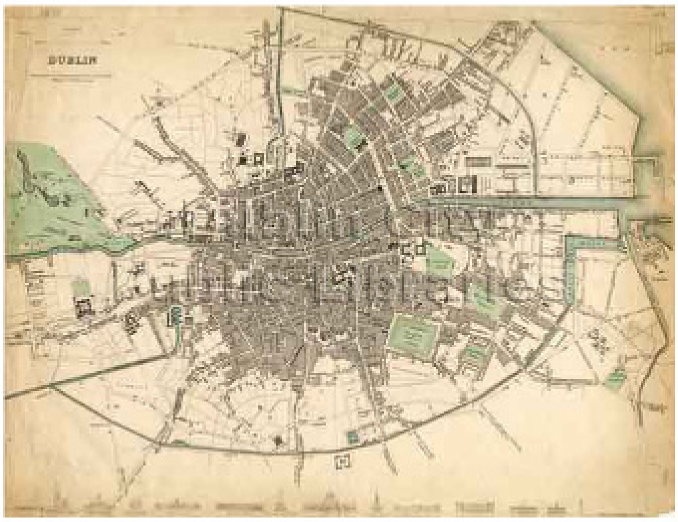
Industrialisation began in Dublin in the mid to late 19th century. Before this time Dublin's economy was driven mainly by administration and commerce rather than industry (National Archives, 2010). It was not industrialised to the same extent as Belfast or the industrial cities of England (National Archives, 2010). Industry was located in the docklands and was related to shipping, exports, and the distribution and processing of imported goods (DDDA, 2010). Imported materials were processed at the docklands in fertiliser factories, flourmills, timber yards and sugar refineries. The docklands were a major distribution and stockpiling centre for imported coal and industries relying on coal grew around the docklands.

Dublin became not only Ireland's capital but Ireland's largest city, greatly exceeding the size of the next largest city (Cork) and becoming the main centre for government, commerce and employment (McManus and Brady, 1994). During the 1960s, Ireland changed from being a predominantly rural society to an urban one, with the percentage urban population exceeding 50% (McManus and Brady, 1994). Rapid expansion of Dublin city followed from the 1970s onwards. The city grew to encompass a wide variety of urban and suburban settlement areas, including highly industrialised areas such as Dublin port, docklands and major industry-supporting watercourses such as the canals and Liffey, Tolka and Dodder Rivers (Carrig, 2011). Urban sprawl unified the core medieval city with suburban areas which initially developed independently of it (Carrig, 2011).



Speed's map of Dublin, 1610

Moll's map of Dublin, 1714



Dublin Street Directory Map, 1833

Figure 3 Historic maps showing Dublin's development in the 17th to 19th centuries. Courtesy of Dublin City Public Libraries.

2.3.2 Historic industry survey

To gain a greater understanding of how past industrial activity may have affected soil quality in Dublin, the GSI commissioned Carrig Conservation and Urban Heritage Consultant Mary McMahon to complete a survey of Dublin's industrial history. The survey recorded the location, nature and operating periods of potentially polluting industries. Sites were identified on historical Ordnance Survey maps and existing industrial heritage data for local authorities in the study area was incorporated.

The survey identified historical industrial sites across the entire study area, though there are significant concentrations within the core city area and along the major waterways (Carrig, 2011).

The docklands were a major centre for 18th and 19th century industry due to their proximity to watercourses for water supply and transportation; access to raw materials imported via Dublin port and for access to the inner city market. The Liberties in particular were a centre for the textile, brewing and animal products industries.

In total 2,022 historic industry sites were identified in Co. Dublin, and these were classified into 10 main categories:

- Minerals and aggregate;
- Metals industry;
- Food industry;
- Textile industry;
- Chemical industry;
- Drinks industry;
- Pulp/paper industry;
- Oil/gas/coal industry;
- Power generation; and
- Animal products.

A description of the nature and occurrences of industries in each category is given below. Maps showing the locations of industries in each category are shown in Figure 4. The significance of these industries in relation to heavy metals and POPs contamination of the soil environment in Dublin is discussed in Section 4.

Minerals and aggregate

Extractive industries featured most prominently in the survey, with 1,081 sites identified in Co. Dublin and some 682 of these sites located within the Dublin SURGE survey area. Extractive industries include quarries, mining operations, gravel pits, lime kilns, sand pits and clay-related activities including clay pits, brick, pipe and tile works. From medieval times to the early 19th century most quarries were minor and/or temporary operations which extracted stone for local building materials (Carrig, 2011). Larger quarries often had associated gunpowder stores and forges for tools. Lime kilns were usually located near limestone quarries and produced quicklime which was used as agricultural fertiliser, as a raw material in blast furnaces, for the purification of coal gas, in the production of bleaching powder and in the tanning process (Carrig, 2011).

Ireland has a long mining history dating back to the Bronze Age. GSI records show that there are approximately 450 mining locations in Ireland, which worked both metallic (Cu, Zn, Fe and Pb) and non-metallic deposits (coal, barite, slate) over time (Stanley *et al.*, 2009). In the Dublin SURGE survey area there are mineral locations relating to lead (12), copper (3), gold (2), iron (2), silver (2) and baryte (1). The historic industry survey identifies historic mining infrastructure at the Ballycorus lead mine and smelting works in south Co. Dublin.

Metals industry

Over 150 forges/smithies, foundries, galvanising works, iron works, brass works, motor and ship assembly works and wire works were recorded in the metals industry category, with over 130 of these in the SURGE survey area. Early ironworks used charcoal-fired furnaces but by the late 18th century most iron works relied on imported coal and were therefore located near to the port (Carrig, 2011). By the end of the 18th century iron works changed from ore smelting activities to recasting cheap cast iron from the UK. Forges or smithies were small scale, local metal workshops which used charcoal, coke or coal as fuel.

Coal and gas industry

Coal was significant in Dublin's industrial past as the dominant fuel in domestic fires, industrial furnaces, steam engines and power generation facilities from the late 19th century to the mid 20th century (Carrig, 2011). Coal was also the primary raw material in the production of coke and coal gas. The coal industry declined in the second half of the 20th century when electricity supply was rolled out across Ireland in the 1950s and with the discovery of natural gas off Kinsale in 1971 (Bunbury, 2009).

Traditionally fossil fuels including wood, peat and coal were burned as domestic fuel in Dublin and the usage of these materials increased as the city grew over some 1000 years. In 1900, a large inner city house would use a ton of coal a month (DDDA, 2010). During the 1980s domestic coal burning reached a peak in Dublin city, causing severe black smoke and smog pollution during that decade (Clancy, 2010). A ban prohibiting the sale, marketing and distribution of bituminous coal came into effect in 1990, after which a 71% decrease in black smoke particulates was observed (Clancy, 2010).

Many industries which relied on coal grew around the docklands and port area due to the reliance on imported coal, including coal merchants, coke ovens, coal gasification works and organic chemical works. A significant portion of these activities were centred on the Grand Canal Dock area. In 1870 there were five glassworks in Ringsend, which used large quantities of coal to manufacture glass (DDDA, 2010). The historic industries survey records indicate in mid-19th to mid-20th century Co. Dublin there were 6 coal yards, with 4 of these located in the docklands.

Coal gas, also known as town gas, was a major factor in 19th century industrial progression (Carrig, 2011). It was derived from coal in a process known as carbonisation involving the distillation of bituminous coal. Coal gas was used to light street lamps and local homes in the 19th century. By-products of the coal carbonisation process included coke (a type of smokeless char used in metalworks furnaces), coal tar (used as a source of organic chemicals), clinker (fused ash waste), lime and ammoniacal liquor (both used to purify coal gas) (UK DoE, 1995a). The historic industries survey indicates that in mid-18th to mid-19th century Co. Dublin there were eighteen gasworks facilities. Four of these were located in the docklands, with major coal gas facilities at Sir John Rogerson's Quay and South Lotts Road/Barrow St.

By-product coal waste materials such as clinker, fly ash and lime were often used as hardcore fill materials at gasworks sites (DoE, 1995a) Such waste materials from the coal industry were also used historically to progressively reclaim land in Dublin's docklands area during industrialisation in the 19th and early 20th centuries.

Power generation

The electricity network was expanded across the country through the establishment of the Electricity Supply Board (ESB) in the 1920s. Electricity generation traditionally relied on the combustion of peat, coal and fuel oils and hydroelectric power. Twenty-five power generation facilities are identified in the greater Dublin area from the late 19th century onwards, from local engine houses to large ESB power stations.

In 2009 the ESB operated 25 power generation facilities in Ireland, of which 10 were run by hydroelectric power; 7 by gas, coal or oil; 6 by wind power and 2 by peat (ESB, 2009). One remaining station at Moneypoint, Co. Clare is coal-fired. There are four power generation facilities in the greater Dublin area. Two ESB stations are located in the docklands area, one at North Wall and one at Poolbeg peninsula. Electricity production ceased at the ESB Poolbeg facility in March 2010. Poolbeg, with its two distinctive smoke stack chimneys, ran on oil or gas in recent times but had a long history of coal-fired power generation stretching back to 1903 (Bunbury, 2009). The independent gas-fired Synergen power generation plant still operates at the Poolbeg site. The North Wall Quay ESB power generation facility was first established in 1949 and also runs on gas or oil. Another independent gas-fired plant operates at Huntstown, Co. Dublin.

Chemical industry

The chemical industry in the 18th and 19th centuries consisted of some 68 mostly small-scale operations located in the docklands near to water supplies from the Tolka and Liffey. Chemical operations recorded include asphalt works, bottle/glass factories, paint, varnish and printing works, vitriol works, chemical/artificial manure works, gunpowder mills, soapworks (and related alkali and sal-ammoniac works). There were three vitriol works in the docklands area which used sulphuric acid for bleaching of linen cloth. Soap and alkali works were located near to textile industries due to the demand for soap in textile processing. Gunpowder was produced in Dublin at several mills in the Corkagh area in southwest Dublin until the mid 19th century.

Phosphorus (P) was a raw ingredient in both match manufacture and chemical/artificial manure works. Early match factories used phosphorus to manufacture match heads. The Maguire and Paterson match factory operated in Hammond Lane off the north quays from 1882 to 1989. Early fertiliser works, which were known as chemical/artificial manure works, extracted P from crushed bones. In the 1870s mineral P began to replace bone in the manufacturing process (Carrig, 2011). There were two chemical manure works in late 19th century Dublin, at Pelletstown and Alexandra Road in modern Dublin port.

Paint/printing works are the most numerous in the chemicals category, with over 20 historical operations recorded in the SURGE survey area. A wide diversity of inorganic and organic chemicals (including heavy metals and petroleum oils) were used in paint, ink and varnish manufacture as pigments, solvents, binders and additives (UK DoE, 1995b).

Textile and pulp/paper industry

Both the textile and pulp/paper industries relied upon plentiful supplies of running water and were therefore located preferentially along the rivers Liffey, Dodder and Camac in south Co. Dublin. The demand for paper following the establishment of an Irish Parliament was the main stimulus for the existence of some 20 paper mills in Dublin during the 18th century (Carrig, 2011).

The textile industry was Dublin’s most important industry in the 18th and 19th centuries, with some 100 sites recorded within the Dublin SURGE study area. There were significant centres of textile industry in Chapelizod and the inner city Liberties area producing woollen textiles, linen, cotton and silk (Carrig, 2011). Both paper and textiles industries use a variety of organic and inorganic compounds in production processes.

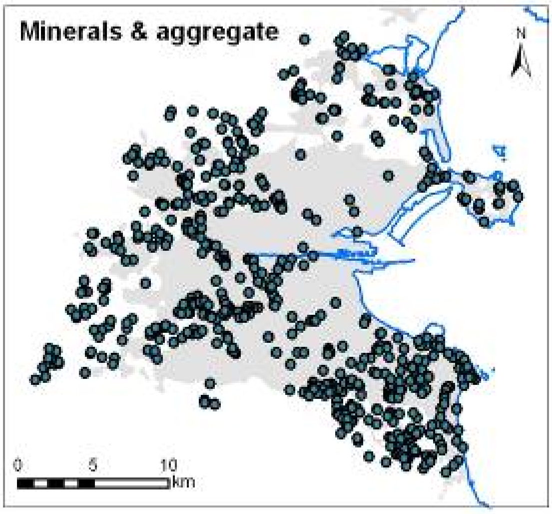
Food and drinks industries

After textiles, the drinks industry was Dublin's second most significant industry, consisting of brewing, distilling, malting and mineral water works. There were over 20 breweries and distilleries in Dublin in the 18th and 19th centuries and the Guinness facility remains one of the largest inner city industrial complexes. The industry relied on watercourses for water supplies and goods transportation and much of this industry was centred on the Liberties area.

The food industry consisted predominantly of wind, steam or water-powered grain and flour mills with over 40 of these sites mainly in inner and south city areas. Bakeries, dairies, warehouses and factories making sweets, biscuits, jam, tobacco products and pork products were also a feature of this industry. Large scale mechanisation of milling in the mid-18th century saw mills located near the port for easy access to coal supplies for fuelling steam engines (Carrig, 2011).

Animal products

From medieval times the Liberties were a centre for industries associated with animal hides, including tanning, dying, skinning, leather production, animal butchery and glue manufacture (Carrig, 2011). In the late 19th century the tanning process used heavy metals and petrochemicals such as phenols, cresols and naphthalene as tanning agents (UK DoE, 1995c). By the end of the 19th century Dublin's tanning industry was in decline (Carrig, 2011).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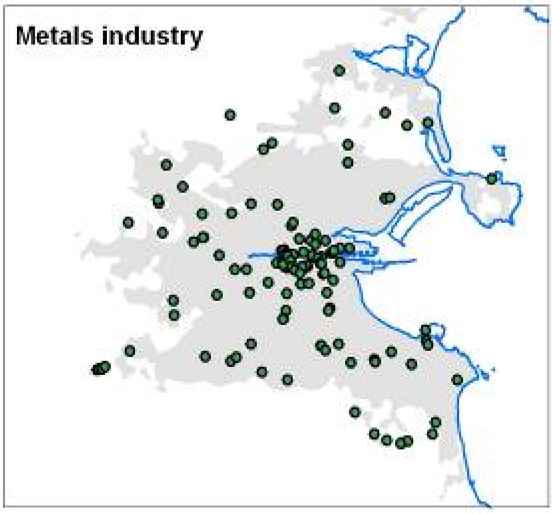
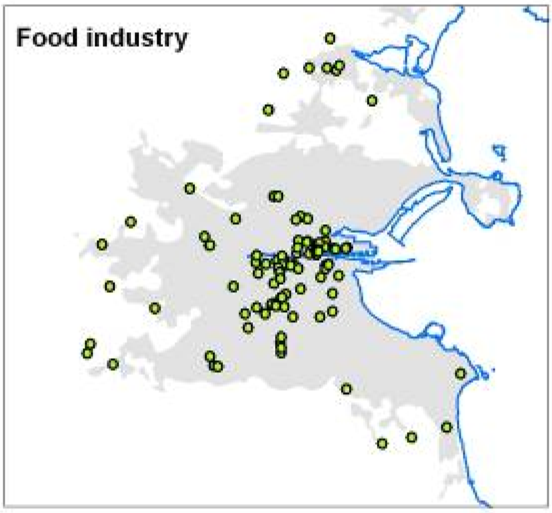
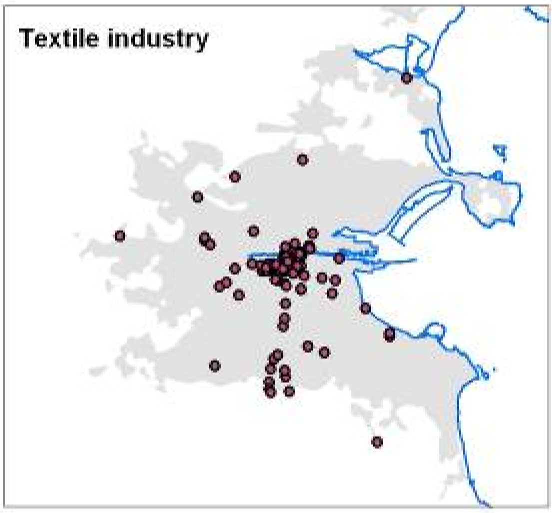
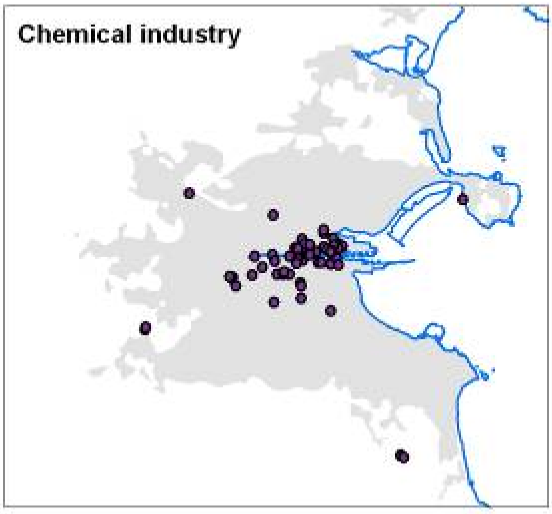
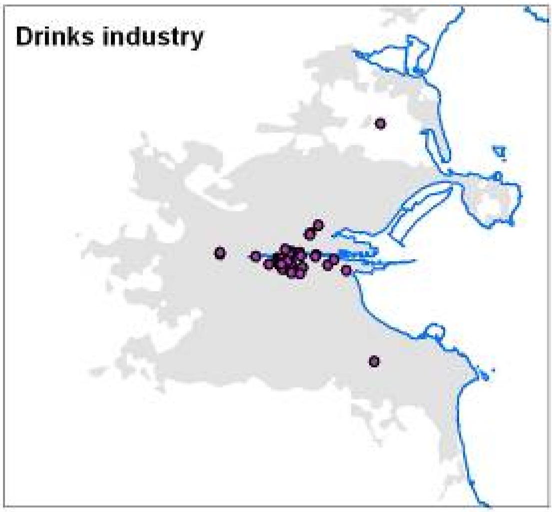

Metals industry


Food industry


Textile industry


Chemical industry


Drinks industry

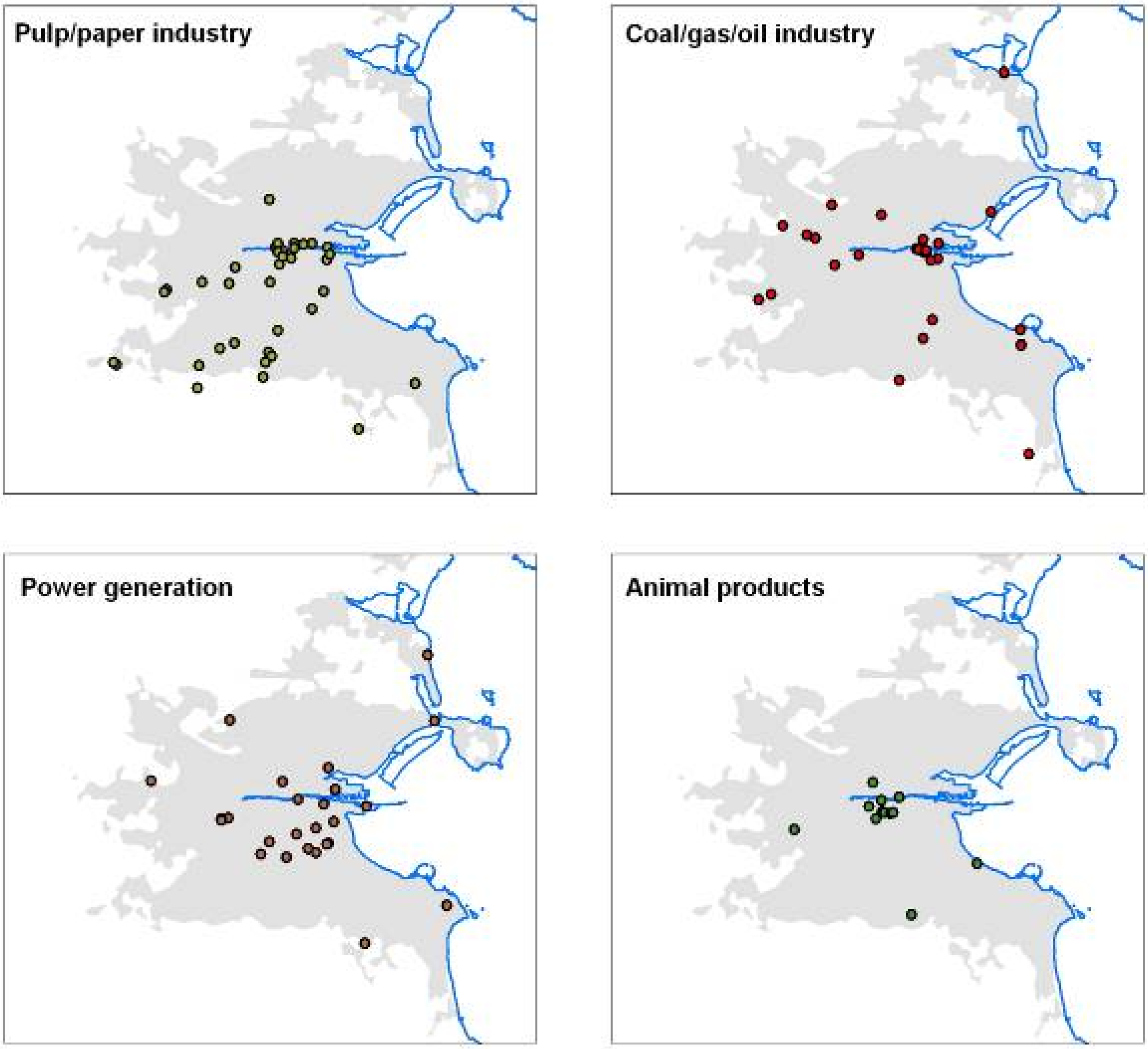
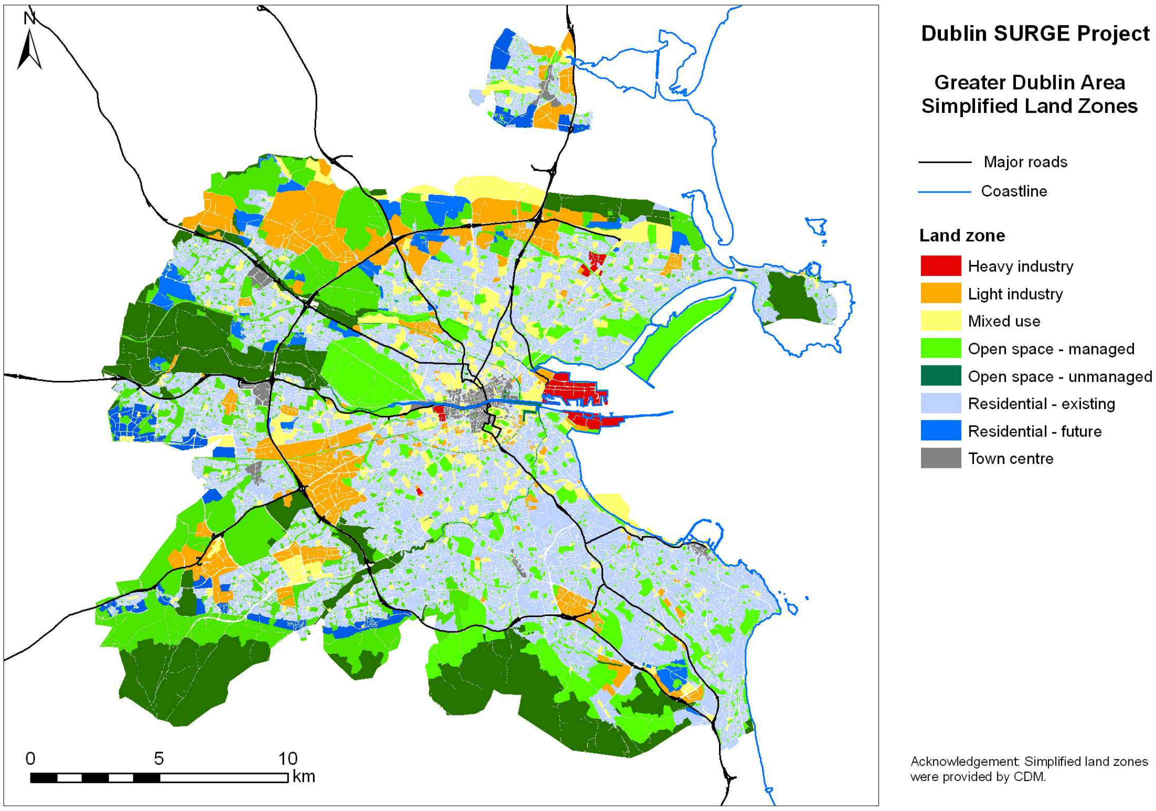


Figure 4 Historic industry locations

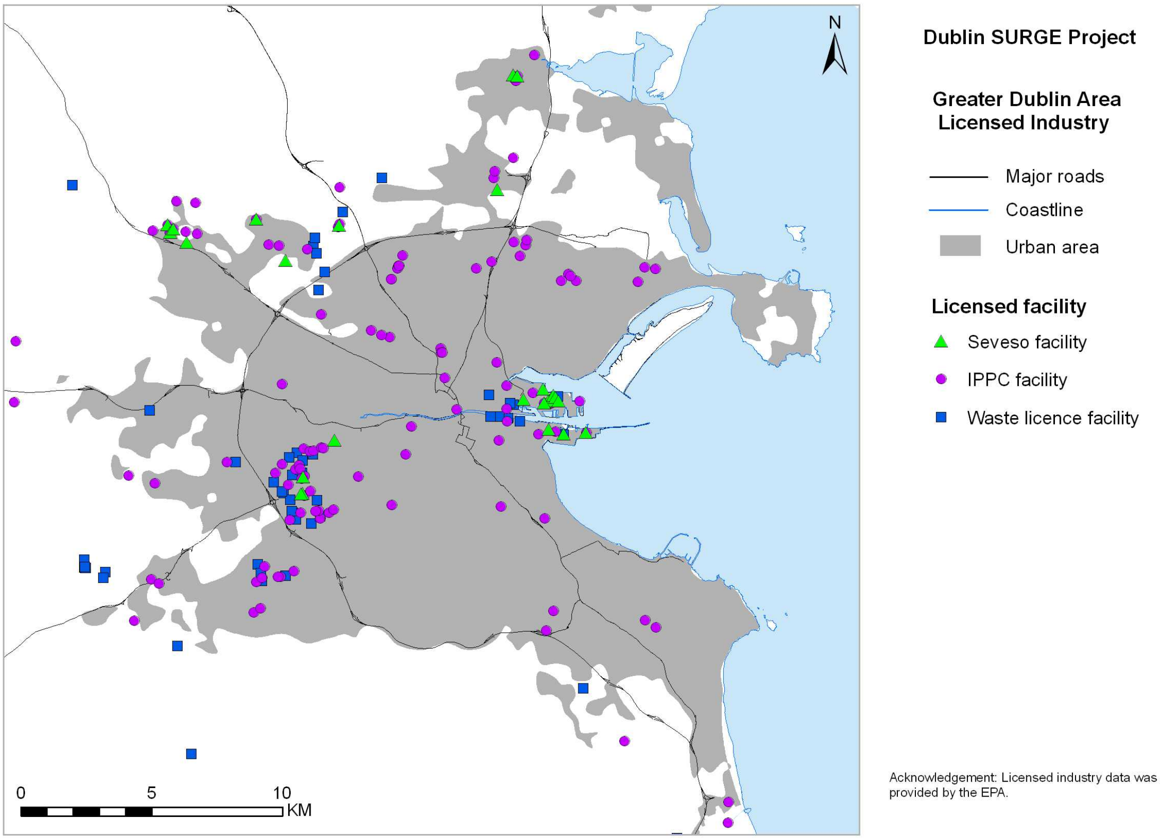
2.3.3 Modern land use and industry

Since World War II the docklands have become a major distribution hub for oil and petroleum, with shipping activities now dominated by container traffic (DDDA, 2010). Apart from the docklands, most industry is now located in designated industrial parks around the periphery of the city and the main ring road motorway, the M50. This trend is illustrated in Figure 5 which shows land zones for the greater Dublin area. The zones are based on county council development plans which were simplified by CDM (CDM, 2009). The map indicates the location and extent of 8 main land zones: heavy industry, light industry, mixed use, open space (managed and unmanaged), residential (existing and future) and town centre.



Acknowledgement: Simplified land zones were provided by CDM.

Figure 5 Simplified land zones for the Greater Dublin area



Acknowledgement: Licensed industry data was provided by the EPA.

Figure 6 Modern licensed industry locations in the Greater Dublin Area

The EPA has been licensing modern large-scale industrial activities in Ireland since 1994 (EPA, 2010). Statutory licensing systems are enforced to avoid adverse environmental impacts from the following industries:

- Industries where dangerous substances are/were present in significant quantities. These industries are subject to “Seveso” licensing under EC Directive 1996/82/EC on the Control of Major Accident Hazards Involving Dangerous Substances (“Seveso” II Directive);
- Industries which emit to environmental media. These industries are subject to Integrated Pollution Prevention Control licensing under the EC Directive 2008/1/EC concerning Integrated Pollution Prevention and Control; and
- Waste disposal activities, which are subject to waste licensing under the Waste Management Act (1996).

Licensed industries in the study area (Figure 6) currently include:

- Chemical manufacturing, storage and supply;
- Distilleries;
- Electricity generation;
- Fuel oil/gas storage and distribution;
- Waste storage, recovery and recycling facilities;
- Pharmaceuticals;
- Rail depots;
- Manufacturing and packaging factories;
- Hospital incinerators;
- Paper milling, printing, inks and paints;
- Aeronautical facilities;
- Metal processing and plating;
- Plastics;
- Timber processing; and
- Asphalt, tar and bitumen works.

2.4 City zones

In order to examine the spatial extent of soil chemical concentrations in Dublin for this study, the city is divided into zones which account for the history and geography of different city areas (Figure 7). Four zones (City Centre, Inner Suburban, Outer Suburban and Rural) are designated concentrically from the inner city outwards, to reflect the progressive outward sprawl in Dublin’s development over time.

The City Centre zone is based on Dublin’s traditional residential and industrial core, representing roughly the extent of the city limits bounded by the Royal and Grand Canals in the mid-19th century. This time corresponds with the beginning of industrialisation in Ireland and represents the area with the greatest concentrations of historic industries in the 18th-20th centuries. The Inner Suburban zone extends to the boundary of the M50 motorway, which corresponds roughly with the extent of the city in the early 1990s.

The Outer Suburban zone includes urban areas outside the M50, including the main satellite towns of Howth, Malahide, Swords, Blanchardstown, Mulhuddart, Lucan, Clondalkin, Tallaght and Dún Laoghaire which now form contiguous urban area with Dublin city. The limits of urban fabric were determined following the CORINE urban morphological zones, which are land cover classes from 2000 considered to contribute to urban fabric and function lying less than 200m apart (Milego, 2007). Such urban fabric includes ports, airports, sports facilities, transportation networks and urban green areas; and water courses and forests when they are contained within urban fabric classes. This dataset was supplemented with information from recent aerial photography (OSI 2006).

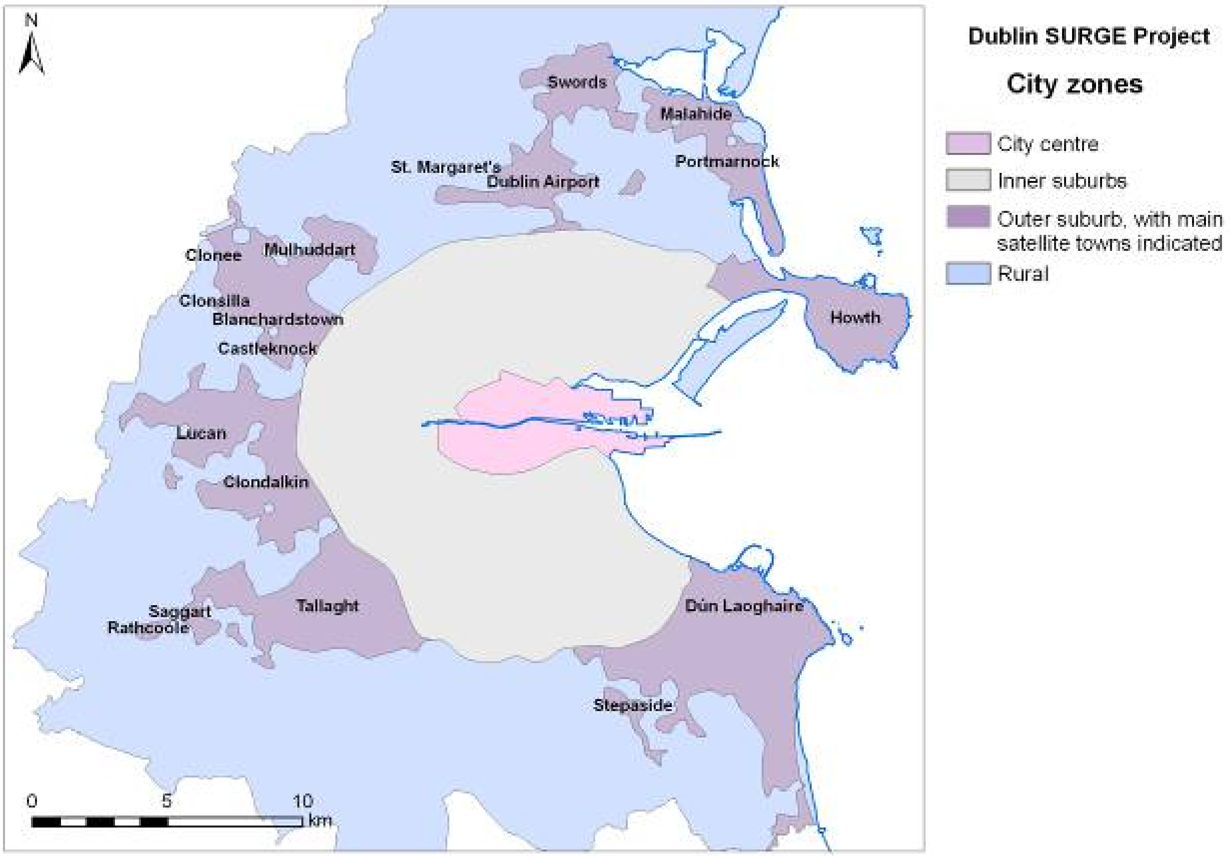


Figure 7 City zones

3 Methodology

3.1 Field work

The aim of the field campaign was to sample soil in locations where members of the public may come into contact with the soil. A random sampling strategy was adopted to give an unbiased overview of soil quality in the city. The sampling did not target or avoid sites of known or suspected contamination.

The study area included lands owned by all four local authorities, namely Dublin City Council, Fingal County Council, South Dublin County Council and Dún Laoghaire-Rathdown County Council. The local authorities provided the GSI with maps of publicly accessible local authority land for sampling. Land uses of such locations included open spaces, road verges, parks, sports grounds, playgrounds and allotments. A total of 1058 samples were taken in the greater Dublin area (Figure 9). Of these 1058 samples, 194 samples were analysed for organic contaminants PAHs and PCBs as well as heavy metals (Figure 10).

Sample locations were generated randomly using GIS software within a 1km^2 grid and were modified to coincide with local authority-owned land. Locations were further modified in the field depending on access restrictions to sites. A number of additional samples were also taken on school grounds and lands owned by the Office of Public Works, University College Dublin and Trinity College. Sampling was completed over a twelve-day period from 22nd October to 3rd November 2009. Up to 4 field teams (from the Norwegian Geological Survey, NGU) of 2 samplers each traveled by taxi to sampling locations each day.

Soil sampling was conducted in accordance with the following EuroGeoSurveys procedure (Figure 8). This approach should allow the direct comparison of studies carried out in different European cities under the wider URGE project.

- Sample collection.
  From each location a sample of 300-500g of surface soil was collected from a depth of 0-10cm with a metal garden trowel or spade. The trowel/spade was free from any paint or material that could contaminate samples. The trowel/spade was cleaned between samples. If grass was present at the sampling location, a knife was used to cut away grass.

- Field duplicates.
  From every 20th sample site a duplicate sample was collected approximately 50 cm apart from the first sample. The duplicate sample was marked sample ID plus D.

- Sample storage.
  A Rilsan® inert, transparent plastic bag was used to store samples. Bags were sealed with a cable tie. A black, water resistant, permanent marker (e.g. PENOL 750) was used to write the sample number on the outside of the sample bag.

- Recording sample location.
  The coordinates of the sampling location were saved in a GPS and written down. Global

Positioning System (GPS) units incorporating Differential GPS and the Egnos/WAAS system was used to determine coordinates (+/-5m for 95% of samples) for all sampling locations.

- Digital photos of sampling sites were taken.

Figure 8 Soil sampling procedure

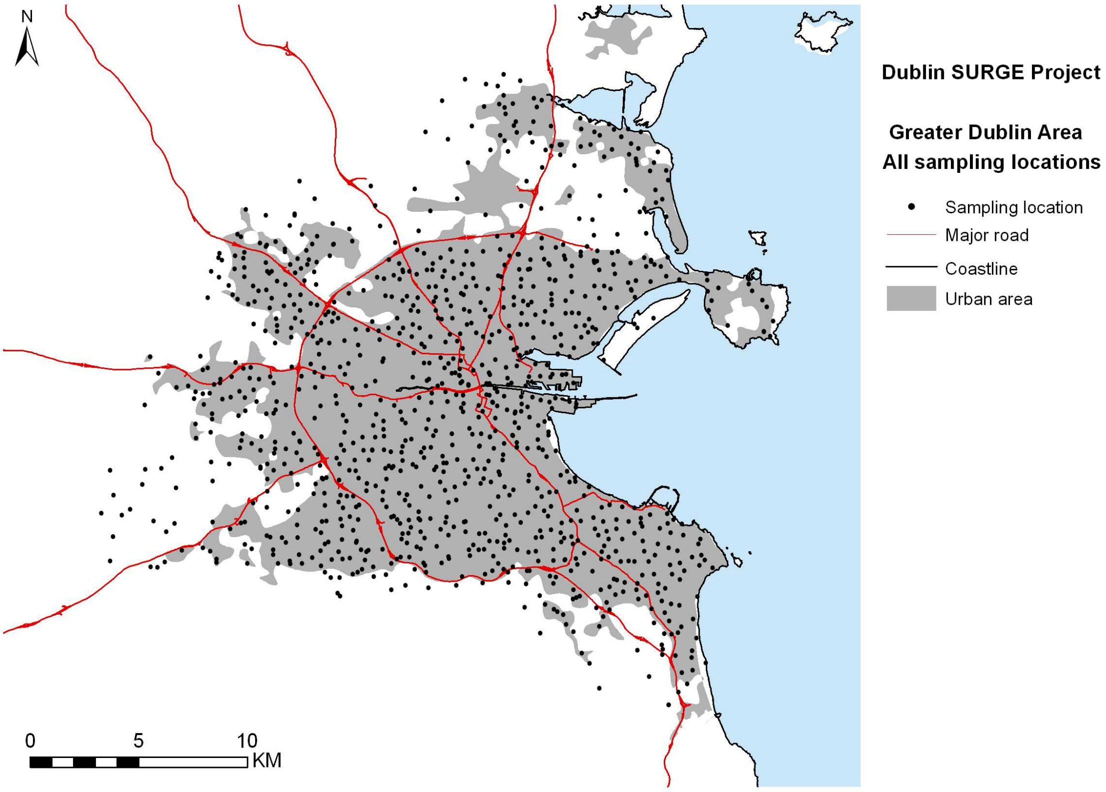


Figure 9 All sampling locations map (n = 1058)

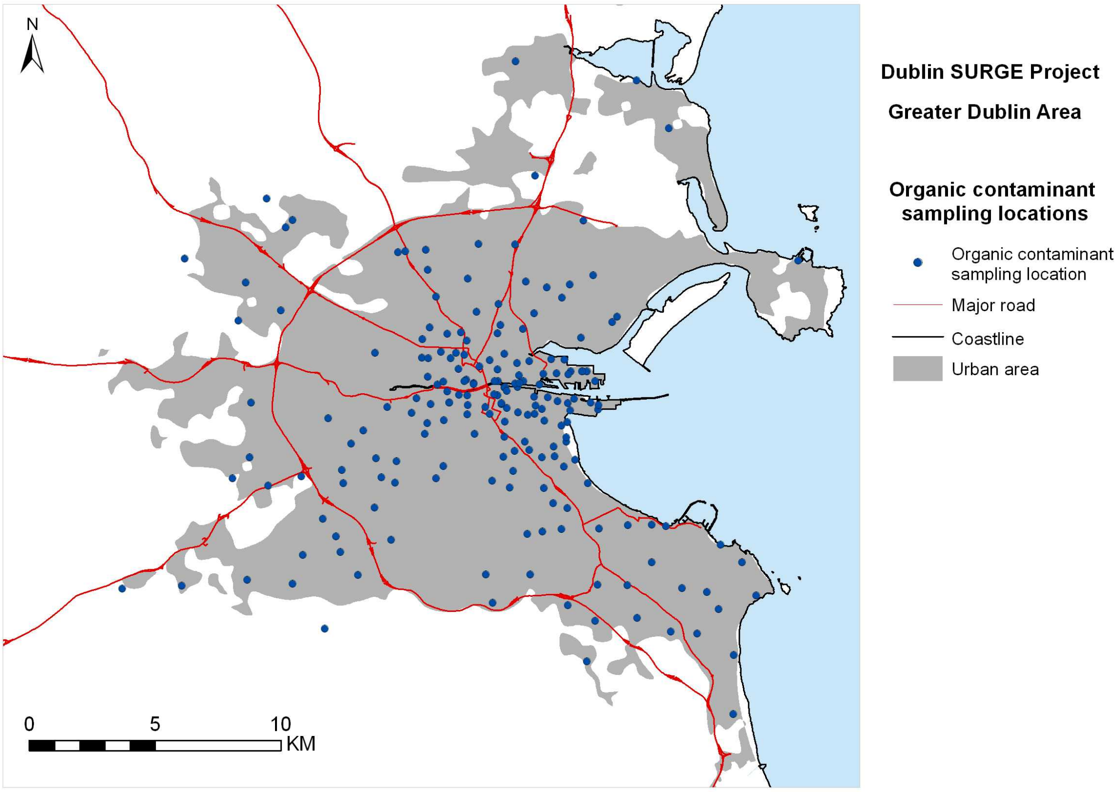


Figure 10 Organic contaminant sampling locations map (n = 194)

3.2 Sample preparation and analysis

All samples were stored at GSI in Dublin, prior to being shipped to NGU in Trondheim, Norway. Samples for PAH and PCB analysis were shipped to an external laboratory, ALcontrol, Sweden for analysis, without any sample pre-treatment.

3.2.1 Inorganic elements analytical technique

The samples for inorganic analysis were air dried at <30ºC/ambient temperature and sieved through a 2mm nylon sieve. The analytical work was undertaken on the <2mm sieved fraction at NGU laboratories. The samples were digested by acid extraction in a microwave system, UltraClave IV, Milestone. One gram of sample material was weighed into a PTFE vessel before 15 ml 7M HNO_3 was added. The mixture was carefully stirred on a Vortex Genie shaker to assure that the sample was completely wetted by the acid. The samples were then heated under nitrogen pressure up to 250 °C.

The acid extractions from the samples were filtered using 90mm diameter Whatman folded filters. The residue consists mainly of silicates that will not be digested unless stronger acids like hydrofluoric acids are used. The method described is a modification of EPA method 3051. The analysis for mercury was carried out with a cold-vapour atomic absorption spectrometer (CV-AAS) instrument CETAC M-6000A Hg Analyzer. The remainder of the elements were analysed with an inductively coupled plasma-atomic emission spectrometry (ICP-AES) instrument Perkin Elmer Optima 4300 Dual View. Loss on Ignition was determined by heating the samples in 480°C for 20 hours.

The method detection limits for the elements are as follows, in mg/kg dry weight:

Al (30), As (3), B (15), Ba (1.5), Be (0.15), Ca (150), Cd (0.15), Ce (3), Co (0.15), Cr (0.3), Cu (1.5), Fe (4.5), Hg (0.0075), K (150), La (0.15), Li (0.75), Mg (150), Mn (7.5), Mo (1.5), Na (300), Ni (1.5), P (15), Pb (3), Sc (0.15), Si (375), Sr (1.5), Ti (1.5), V (1.5), Y (0.15), Zn (3) and Zr (3).

3.2.2 POPs analytical technique

Analysis of soil samples for PAHs and PCBs was carried out at ALcontrol Sweden, which is accredited to the ISO 17025 international standard for laboratory analysis. Determination of the 16 EPA PAH compounds was carried out using gas chromatography – mass spectrometry (GC-MS). Ten grams of the soil samples were weighed and extracted using a 1:1 volume mixture of acetone and n-hexane. The method detection limit (MDL) was 0.03 mg/kg dry weight.

Determination of the 7 PCB congeners was carried out using gas chromatography – electron capture detector (GC-ECD). Ten grammes of sample material were weighed and extracted using a 1:1 volume mixture of acetone and n-hexane.

Three different method detection limits were reported for PCB results. The standard analytical method was GC-ECD, with an MDL for individual congeners of <0.003 mg/kg. Laboratory notes stated that due to interference in a number of samples, the analysis of these samples was conducted by GC-MS (with higher detection limits). For three samples the MDL was <0.05 mg/kg for individual congeners. For five other samples the MDL was <0.01 mg/kg for individual congeners.

Interference is due to effects of sample characteristics on the test method execution, such that reliable data cannot be generated. Examples of sample characteristics which may cause interference include extremely high or low pH, chemical constituents that react with target analytes and the presence of a non-target compound in high concentrations. In the latter case the sample would require dilution in order to prevent contamination of instrumentation.

3.3 Quality assessment

The quality assessment process entailed several procedures during field, sample preparation and analysis, which are described below for inorganic elements. Quality assessment procedures were not carried out for organic contaminants results.

3.3.1 GPS coordinates

To reduce the effects of GPS device malfunction, operator errors or poor dilution of precision (DOP) values ("urban canyon" and satellite geometry), all recorded GPS positions were checked in a GIS against orthophotos and field photos. An estimate of position error is reported for each data point, with an average error of 10m. This relatively high average value is mostly due to about 5% of the coordinates (almost all in rural districts) being given an error estimate of 100m for confidentiality reasons.

3.3.2 Reproducibility

Field teams collected duplicate samples from 30 of the primary sampling locations throughout the area. The duplicates were sampled concurrently with the primary samples, by the same team, but from a separate pit typically 1 – 10 m apart from the primary location. The samples were treated as primary samples in the workflow. Scatter plots comparing the primary and duplicate analytical results are shown in Appendix A.

In the scatter plots, the results of the primary samples are plotted along the X-axis, and the duplicates along the Y-axis. Ideally, the points should plot along a diagonal line through 0,0, indicating agreement between the primary and duplicate results. Deviations from this line give a graphical display of the sum of errors involved with almost all steps from field to report. The r^2 value is included in each of the plots, providing a number for each variable for comparison of curve fit, but the shape of the point swarm is just as important when evaluating reproducibility. One point alone in a relatively small population can influence the calculated r^2 considerably, reducing r^2 if it is off a general correlation trend, or falsely increasing r^2 if it is far out along the diagonal and the rest of the population forms a cloud with little correlation at much lower average values.

A better understanding of the relationship between primary and duplicate samples is gained by deleting one or two outlying points from the dataset. An example of this procedure is shown in the scatter plot for Pb. It must, however, be taken into consideration that the matrix sampled is urban soil, which is more heterogeneous than natural soil. Hence, a larger error margin should be expected, and geographical clusters should be emphasised rather than single points only.

All elements show acceptable reproducibility. No plots are made for Si, as the procedures are not certified for HNO_3-extraction of geologic material. No further processing is carried out on Si. One of the field duplicates (see plot for Ba) shows high deviation for a number of elements. A repeated weighing, extraction and analysis of the pair confirmed the deviation.

3.3.3 Systematic errors

The time span from start to finish of the preparation and analysis of a 1000+ sample set is quite lengthy, and increases the chance of systematic errors occurring during the extraction and analytical steps. To monitor analytical levels throughout the data set, in-house NGU natural material standards were introduced throughout the sample batch prior to extraction. These standards are two marine sediments, Hynne and KDF, of which the latter is heavily contaminated by As, Cu, Pb and Zn, and three different splits of an overbank sediment sample (Nidelv X) with low to moderate concentrations of the elements of interest for this study.

A visual inspection of the graphs of element versus sequence number (Appendix A) gives no indication of apparent shift in reported level of either of the in-house standards. Some materials display larger and more frequent but random variation, typically the Nidelv samples. Other plots show less uniform results than the others, e.g. Mo in the KDF samples. These are all considered a function of the degree of heterogeneity of the sample material, and not an indication of a systematic error.

When assessing the results of the standard samples as described above, no elements indicate systematic errors.

3.3.4 Accuracy

As part of its own quality assurance system, the lab at NGU inserts certified reference material (CRM) at regular intervals in the analytical batch, providing data for evaluation of the accuracy of the results. The lab reports its results for the CRMs using statistical descriptors, in accordance with accredited routines. These are presented in Tables A1-A3 in Appendix A. The certificate values refer to total content; a negative deviation indicates the less than 100% extraction efficiency.

As a rule, results with relative standard deviation (RSD) higher than 10% should not be considered satisfactory. Ti, Cd and Zr all show slightly higher values, but the results are accepted since the HNO_3-extraction of the CRM yields only very low values compared to the detection limit. The reported values for Mo give rise to an unacceptably high RSD. Uncertain accuracy for Mo is the consequence; even though field duplicates show acceptable reproducibility. Due to the lack of accuracy information, Mo is left out of further processing.

3.4 Deriving geochemical baselines

3.4.1 Basic statistics

The median is used as a measure of central tendency of the dataset instead of the mean as it is not adversely affected by the existence of extreme outliers, which are common in geochemical data. The term outlier is used to refer to a value in the dataset which deviates from the majority of the data (Reimann *et al.,* 2008). The median is not reliable when more than 50% of the data is below the limit of detection for the analytical method (Reimann *et al.,* 2008).

To map the results, results are divided into percentile groups. Percentiles divide the data in such a way as to display the value of a variable below which a certain percentage of observations fall. For example if the 90th percentile level of a dataset is 100 mg/kg, this implies that 90% of the data does not exceed 100 mg/kg and only 10% of the data is greater than this level.

3.4.2 Exploratory data analysis

A number of exploratory data analysis (EDA) tools are used to help illustrate the nature and extent of elements and organic compounds in soil – the histogram, the cumulative probability (CP) plot, the boxplot and the scatter plot matrix.

Histogram

The histogram shows the distribution of the data, or the frequency with which data values occur in the dataset. Normally distributed data show a classic “bell-curve” shape, indicating that most data lie within a central range, with few very low or very high values. Geochemical data is often right-skewed on the histogram, meaning that there are often outliers which are much greater than the main body of the data (Reimann *at al.,* 2008). In this study where data is right-skewed, the histogram is plotted on a logarithmic scale so the main body of data is “stretched out” and more easily visualised. An example is shown in Figure 11. Histograms for each element or compound are shown on the main map page for each element/compound.

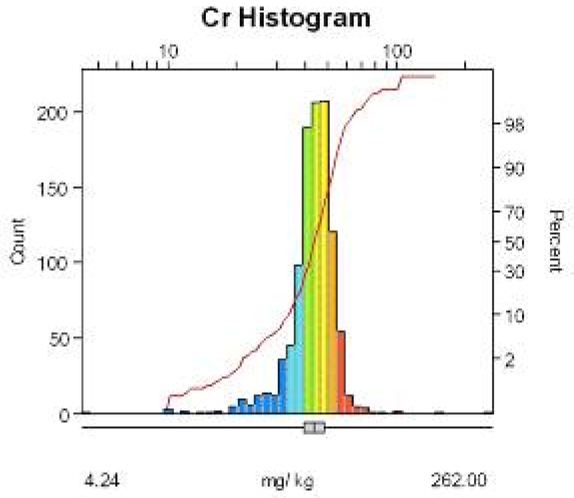


Figure 11 Log-scaled histogram with CP plot for Cr.

The cumulative probability (CP) plot

The CP plot, the red line shown in Figure 11, shows the frequency of occurrence of any value on the x-axis as a percentage on the y-axis. The CP plot in Figure 11 shows two y-axes, the number of samples in each histogram category on the left and the cumulative probability percentage on the right. This axis is distorted in such as way as to stretch out the very low and very high values, and to contract central values such that normally distributed data will plot as a straight line. Breaks or kinks in the line can indicate that part of the data follows a different distribution than that of the rest of the data.

The boundary between distinct data populations can be utilised to separate the natural background from the anthropogenic contribution in trace element concentrations. In this study, CP plots are shown superimposed as a red line on the histogram for each analyte. In the example in Figure 11 the upper break in the CP plot at occurs between 50 mg/kg and 60 mg/kg, which is taken as the upper limit of the natural baseline for Cr. Concentrations of Cr above this level are expected to be related to anthropogenic contamination.

Due to heterogeneities in urban soil, occasionally a single distinct break is not clearly identifiable and the natural baseline is reported as a range or as an approximate figure. This may also be due to overlapping mixtures of data from several different populations.

The boxplot

The boxplot is a graphic which visualises the data using a box to represent the main body of data within the 25th to 75th percentiles. The distance from the 25th to 75th percentile is known as the interquartile range. Outliers are represented by their distance from the box by whiskers and symbols. The parameters used for the boxplot were established statistically by Tukey (1977, cited in Reimann *et al.,* 2008) and are shown in Table 1 and **Error! Reference source not found.** Although the Tukey boxplot is designed to illustrate normally distributed data, it will not be seriously disturbed up to 25% outliers at either end of the distribution (Reimann *et al.,* 2008).

In this study the boxplot is used to visualise how median concentrations of soil chemicals change with different city zones, land uses, soil types and bedrock types. This is done by dividing the data up by category and plotting side-by-side boxplots for each data type. Where side-by-side boxplots for different types of data show that their boxes do not overlap (the central 50% of one type does not overlap with the central 50% of the other type) this may indicate different populations of data (BC Environment, 2001).

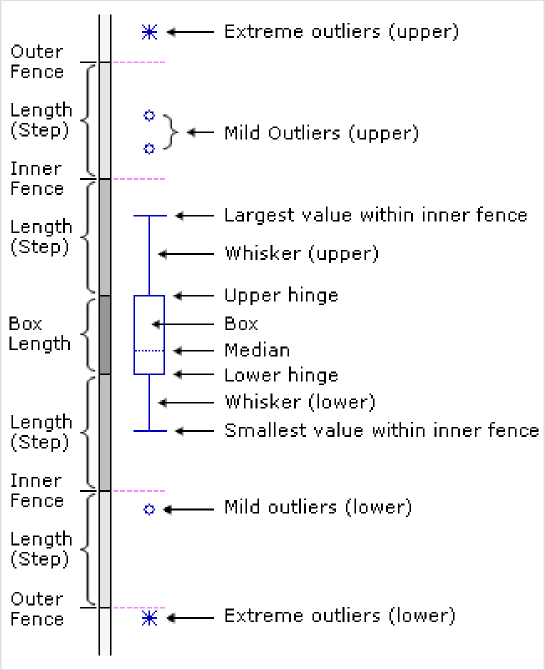


Figure 12 Box plot component descriptions

The scatter plot matrix

The scatter plot matrix allows visualisation of the relationships between the inorganic elements and the strength of these relationships. The matrix shows a scatter plot for each variable against the others, along with the Pearson correlation coefficient for the relationships. The correlation coefficient estimates the strength of the relationship between a pair of variables, which is expressed as a number between 0 and 1 (0 indicates no relationship and 1 indicates a perfect relationship). The coefficient can be positive or negative depending on the nature of the relationship (a negative correlation indicates an inverse relationship, and a positive correlation a positive one). Log-scaled data is used in the scatter plot to reduce the influence of outliers. The value of the Pearson correlation coefficient is shown at the 0.95 significance level, with colour-coded relationship strength categories:

- <0 : No relationship (grey)
- 0.1 – 0.2: Very weak (blue)
- 0.2 – 0.4: Weak (green)
- 0.4 – 0.6: Moderate (orange)
- 0.6 – 0.8: Strong (red)
- 0.8 – 1.0: Very strong (pink).

3.5 Derivation of rural baseline from National Soil Database samples

The geochemical baseline is a function of the methodology used to derive it, i.e. environmental medium (topsoil, subsoil, etc), sampling method, sample preparation and analytical method (Johnson & Ander, 2008). Baselines for different cities may only be compared like-for-like if the methodology is the same or if datasets are levelled to account for differences in the methodology. On this basis, the Dublin SURGE

Project is not directly comparable with existing geochemical studies which have been carried out in Ireland.

Despite this, it is desirable to compare the SURGE results to a rural baseline in order to better understand how the urban environment is enriched with trace elements compared to the rural environment. There are significant differences in analytical methods which the SURGE and Soil Geochemical Atlas surveys used, therefore soil results they cannot be directly compared. However, it was possible to retest a subset of NSDB soil samples using SURGE analytical methods in order to create a rural baseline dataset which is comparable to SURGE.

Element of boxplot:	Calculated by:	Represents:
Upper hinge (Top of box)	75th percentile level	Upper boundary of main body of data
Lower hinge (Bottom of box)	25th percentile level	Lower boundary of main body of data
IQR (Length of box)	75th percentile level - 25th percentile level = interquartile range (IQR)	Main body of data
Line in centre of box	50th percentile level	Median
Inner fence (Upper whisker)	IQR + (1.5 x IQR)	Boundary above which values are considered mild outliers (circle symbols)
Outer fence (Change in symbols)	IQR + (3 x IQR)	Boundary above which values are considered extreme outliers (star symbols)

Table 1 Elements of the Tukey Boxplot (Reimann *et al.,* 2008)

With the permission of Teagasc, eight NSDB soil samples taken in the rural outskirts of the greater Dublin area were retested along with SURGE samples. The results from the SURGE analysis were consistently lower than the original Soil Geochemical Atlas results, which is likely to be due mainly to different extraction methods used in the analytical processes. The Soil Geochemical Atlas project used a strong acid (hydrofluoric acid) for the extraction of trace elements from soil samples. Hydrofluoric acid decomposes most siliceous minerals, resulting in a near-total extraction. The SURGE project used a less aggressive extraction using nitric acid.

Although the SURGE analysis returned lower results, it is possible to demonstrate that these results are proportionate to the results obtained in the Soil Geochemical Atlas using scatter plots. Scatter plots of concentrations obtained in the two surveys (Appendix B) show that the different extractions used give consistent results. The r^2 values are >0.9 in most cases indicating excellent correlation between the two surveys. NSDB values quoted in this report are those which were retested as part of the SURGE project.

3.6 Comparison with other cities

Although it is not possible to directly compare results from the Dublin SURGE Project with urban geochemical surveys carried out in other cities, results from other cities can be used to put the Dublin results into a broad context. For PAHs, PCBs and anthropogenic heavy metals results, data for other cities is included for reference only.

3.7 Mapping

In order to ensure the confidentiality of individual sites sampled as part of SURGE, maps are presented in such as way as to protect the exact location of individual sites. The preferred mapping method is interpolation, where contoured surfaces are generated from point values. Various interpolation methods are available which range from deterministic to statistical approaches. Statistical methods such as kriging are not exact but produce a surface which takes into account the relationship between point values in space, allowing a smoothed representation of the modelled data. For inorganic elements, ordinary kriging was used to contour the data.

For PAHs, contouring was more difficult due to the underlying discontinuous processes which influence the deposition of PAHs in the environment. Inorganic elements are heavily influenced by a single underlying process – the weathering of parent bedrock material – which means that spatial autocorrelation (the relationship between data values in space) is generally good. However, PAH deposition is influenced by a variety of anthropogenic activities meaning that spatial autocorrelation between data values can be low. Hence a continuous surface is difficult to approximate and the results for PAHs are presented as points (each representing approximately 250m point diameter on the ground) on a simplified background showing only the urban area of Dublin.

4 Soil geochemistry

This section outlines the nature, occurrence and behaviour of persistent organic pollutants and heavy metals in soils.

4.1 Inorganic elements

Ninety-nine percent of the earth's crust is made of 8 major elements – O, Si, Al, Fe, Ca, Na, K and Mg (Thornton, 1983). Concentrations of elements in soil are strongly influenced by the composition of underlying geology. This principle has been used as the basis of geochemical exploration for many years. Through soil surveys for geochemical exploration it was realised that soil chemistry can also be influenced by human activities, especially in urban areas.

Soil samples were tested for 31 inorganic elements which encompass the major elements and trace elements found in soils. Inorganic elements which occur naturally in soils are derived from the weathering of rock parent material. Human activities can cause enrichments of inorganic elements, especially heavy metals, in soils (Section 4.2.). Soils act as a sink for heavy metals in the environment, since they bind readily with soil organic matter and clay particles (McGrath & Smith, 1990). Compared to air and water, little mixing and dilution of metals occurs in soils, meaning that they are persistent and relatively immobile in the soil environment (McGrath & Smith, 1990). Topsoils tend to have higher concentrations of metals derived from human activity than other soil horizons due to atmospheric deposition and abundant organic matter (Alloway, 1990).

Heavy metals can exist as many different phases within soil: bound in soil minerals, adsorbed to soil particles, bound to soil organic matter or dissolved in soil pore water (Jeffries & Martin, 2009). The existence of and relationships between these phases are complex and determined by soil conditions and chemical properties (Jeffries & Martin, 2009). In general, most metals become more soluble and bioavailable in acidic conditions (Alloway, 1990).

4.2 Anthropogenic sources of metals

Anthropogenic enrichments of heavy metals in soils can give rise to concern for human health (Section 5). Activities which can emit heavy metals to the environment are described below, with reference to relevant historic industries in Dublin.

Mining and mineral abstraction

Mining and mineral abstraction involve the abstraction of materials such as fuels (coal and oil), aggregate, minerals and metal ores from the ground. Waste materials resulting from the separation of metals from their ores are a serious source of environmental contamination (Fuge, 2005). Tailings are the fine material left over from the crushing and grinding of ores. Tailings piles can contain high residual levels of heavy metals which can become mobilised into the environment by wind and runoff, especially at old, abandoned mine workings (Fuge, 2005).

According to a study carried out by the GSI and EPA, Pb is the most significant contaminant in and around Irish historic mine sites (Stanley *et al.*, 2009). The study ranked 27 priority historic mining sites in Ireland according to their risk to human health. Of the sites ranked, one lies within the Dublin SURGE Project study area, at Ballycorus in south Co. Dublin, which operated until the mid-20th century. Lead and silver were mined and smelted at the historic mine workings at Ballycorus in south Co. Dublin, where exposed waste piles remain at the site with high concentrations of Pb (median values exceeding 1.5%) (Stanley *et al.*, 2009).

Metalworks

Metalworks is a broad term which encompasses processes such as the primary production of metals from ores (smelting and refining), alloying of metals (e.g. steelworks), recasting (foundries) and metal finishing (e.g. electroplating).

Smelting is a process which purifies metal ores by roasting them at high temperature, which produces atmospheric emissions of gaseous sulphur dioxide, aerosols and metallic particulates; and blast furnace slag (Fuge, 2005). Refining removes further metallic impurities from the smelted metal using pyrometallurgical, electrolytic or chemical processes (UK DoE, 1995d). Although modern smelters have dust recovery mechanisms, older smelters often emitted high concentrations of particulate metals in the direct vicinity and downwind of smelters (Fuge, 2005). Smelting and refining were often located at mining sites or in ports due to the proximity to sources of metal ores and furnace fuel (i.e. imported coal). This is reflected in Dublin by the clustering of historic metalworks sites around Dublin port and docklands and by clustering of Pb smelting operations at Ballycorus Pb mine in south Co. Dublin.

Steel is an alloy of Fe, carbon (C) (<2%) and Mn (<1%); stainless steel also contains 8-25% Cr (UK DoE, 1995e). Wastes produced from the steelmaking industry include slag and metal slurry or dust from furnace cleaning, often containing As, Cr, Mn, Mo, Ni, Fe, Pb and Zn (UK DoE, 1995e). Metals commonly used in plating processes include Cu, Cr, Ni, Zn, Cd, Sn (tin), Pb, Ag and Hg. Contamination may result at metal plating and other metal finishing operations from leaks, spills or on-site disposal of raw materials, process materials and waste products (UK DoE, 1995f).

Coal, oil and gas industry

Trace elements in fossil fuels are released into the atmosphere or retained in ash upon combustion (Fuge, 2005). Trace element geochemistry depends on the type and source of the fuel; for instance European coals are associated with As, Cd, Cr, Cu, Ni, V and UK coals contain significant amounts of Pb (Fuge, 2005). Ash from coal burning processes, known as fly ash, is a finely powdered glass-like substance which can contain many heavy metals including As, B, Ba, Cd, Cr, Cu, Pb, Mo, Ni, Se (selenium) and Zn (UK DoE, 1995a).

The coal industry was a major part of Dublin's industrial development (Section 2.3.1), which was centred on the docklands area. Many industries which relied on coal for power generation were established in the area during industrialisation, including municipal power stations, textile mills, breweries, food manufacturing and the pulp/paper industries. Impacts of coal burning on air quality were addressed in Dublin in 1990 with the bituminous coal burning ban. Similarly land contamination at many former gasworks sites has been extensively remediated. However it is expected that point source heavy metal contamination may remain at some sites due to contamination from coal related operations and the use of coal combustion wastes such as clinker and ash as fill in low-lying areas of the city, particularly in the docklands, coastal areas and the inner city.

Cement, lime and fired clay production

The firing of limestone in the production of cement and lime, and the firing of clay for brick, pipe, pottery and ceramics releases trace elements including Cd, Cr, Cu, Pb, Hg, Ni and Zn (UK DoE, 1995e). Lime kilns were very common in Dublin's industrial history, with some 77 lime kiln sites recorded in the SURGE study area as part of the historic industries survey, mostly located in central and south Dublin. Some 25 clay pits and brick, pipe and pottery works operated in Dublin in the same area. These operations may have contributed to the atmospheric deposition of trace elements and anthropogenic heavy metals such as Pb, both through the burning of fuels such as charcoal, coke and coal and the firing of limestone and clay.

Transportation

It is estimated that 75% of environmental Pb is sourced from vehicle exhausts (Fuge, 2005). Unleaded petrol was introduced in the 1980s in Ireland and the phasing out of leaded petrol was completed in 2000. During the phasing-out period, ambient Pb levels dramatically decreased and have remained low since 2000 (EPA, 2009a). Ambient Pb levels improved in most in inner city locations with heavy traffic burdens (EPA, 2009a). However, Pb is environmentally persistent and high concentrations of Pb due to leaded petrol may remain in roadside and inner city locations.

Vehicles provide other sources of metal contamination, including Zn in tyres and galvanised engine parts, Cd in tyres and lubricating oils, Cr in steel alloys and chrome plating, Cu from brakes and copper wiring, and platinum group elements from catalytic converters (Fuge, 2005). Engine and tyre wear causes particles of these metals to accumulate in road dusts and roadside soils.

Chemical works

Chemical works can involve a large variety of chemicals, however significant industries for metal contamination include paint and printing works, explosives manufacturing and pesticide manufacturing. Over 20 historical printing/paint operations were recorded in the survey area, mainly in the inner city. Compounds of the metals antimony (Sb), Cd, Cr, Cu, Zn, Pb, Ni, Sr and Zn were used as pigments in the printing, paint and ink industries (UK DoE, 1995b).

Also of significance in historical Dublin were artificial manure works and match factories, which used P as a raw material in their manufacturing processes. The anthropogenic, inner city pattern of P concentrations seen in Dublin may be related to these industries, as well as the use of P fertilisers in public areas.

Tanneries

Heavy metal compounds were historically used in the leather tanning process, including Cr as a tanning agent, As as a biocide as well as Mn, Ti and Cd compounds in leather processing (UK DoE, 1995c). The Liberties area on the south quays in Dublin was historically a centre for tanning activities, with some 8 tanneries located in that area until the early 19th century. Although there is no obvious enrichment of these metals in the immediate vicinity of the Liberties, concentrations over the median level for As, Cd, Mn and Ti occur in the area due to its inner city location.

Fertiliser and pesticide production and use

Both fertilisers and pesticides can contain high levels of trace elements and heavy metals. Arsenic was historically used as a pesticide and wood preservative in copper chromated arsenic (CCA) wood treatments. Wood treated with such preparations remains a source of heavy metals in the environment. Modern phosphate fertilisers are a significant source of heavy metals in rural areas (Alloway, 1990) and may also be significant in urban parks where used.

Other activities

Other activities which can potentially cause metal contamination include:

- Sewage sludge from domestic and industrial sources can contain potentially harmful elements including heavy metals. These can pose an environmental risk when sludge is disposed of through landspreading (Fuge, 2005):
- Metal recycling and scrapyards;
- Uncontrolled landfilling of waste containing heavy metals.

4.3 Persistent organic pollutants

Persistent organic pollutants (POPs) are toxic organic compounds which do not readily break down in soil, air or water and they can be taken up by plants, animals and humans in the food chain. POPs include compounds such as PAHs, PCBs, dioxins, furans and pesticides. PAHs and PCBs are amongst the most common POPs.

4.3.1 Polycyclic Aromatic Hydrocarbons

PAHs are complex organic chemicals which consist of two or more benzene rings linked by carbon bonds (C_xH_x) (ATSDR, 1995a). They occur naturally in oil, coal and tar deposits and as a result of volcanic emissions and vegetation fires. Anthropogenic activities are the main source of PAHs in the environment, through incomplete combustion of carbon-containing materials such as fossil fuels and organic waste (ATSDR, 1995a). PAH concentrations are typically higher in urban soils than in rural soils due to the intensity of human activities in cities. Across the UK, PAH concentrations in urban and industrial areas are 5-8 times that of those in rural areas (UK EA, 2007).

There are over 200 known PAH compounds and in this study 16 PAHs, identified as priority pollutants by the US EPA (US EPA, 2009), are considered:

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo(a)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(g,h,i)perylene
- Benzo(k)fluoranthene
- Chrysene
- Dibenzo(a,h)anthracene
- Fluoranthene
- Fluorene
- Indeno(1,2,3-c,d)pyrene
- Naphthalene
- Phenanthrene
- Pyrene

The chemical structure, molecular weight and chemical formula for each PAH compound are given in Table 2. Seven of these compounds are considered potential human carcinogens (Section 5.4).

PAHs are some of the most common organic contaminants in the environment and they occur in soils due to diffuse (widespread) and point (localised) sources of contamination. Emission sources are considered either pyrogenic (from combustion) or petrogenic (from petrochemicals such as petrol, diesel, kerosene, lubricating oil).

The molecular structure of individual PAH compounds, together with local environmental conditions, determines the behaviour of PAHs in the environment in terms of their persistence, solubility and toxicity (ATSDR, 1995a). PAHs are grouped into low and high molecular weight PAHs to describe their fate in the environment. High molecular weight (202 – 278 g/mol) PAHs have four or more benzene rings, including fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene. Low molecular weight PAHs (128-178 g/mol) have 2-3 benzene rings and include acenaphthene, acenaphthylene, anthracene, naphthalene, fluorene and phenanthrene. Low molecular weight PAHs are formed at low to moderate temperatures such as during domestic coal and wood combustion; while high molecular weight PAHs are formed at high temperatures, such as in vehicle combustion engines (Banger *et al.,* 2010).

High molecular weight (HMW) PAHs adhere strongly to organic carbon in soils and black carbon particulates in the atmosphere, which protects them from degradation processes and allows them to persist in the environment. HMW PAHs will gradually degrade in soils due to abiotic and biotic processes, loss to the atmosphere through volatilisation (evaporation) and bioaccumulation in plants over weeks to months (ATSDR, 1995a), depending on environmental conditions.

Climatic conditions such as humidity and rainfall influence fate of PAHs in the environment. Sorption of PAHs to particulates decreases with increasing humidity and dry deposition can be more significant than wet deposition in removing particulates from the atmosphere (ATSDR, 1995a). Dublin's mean annual relative humidity ranges from 74% to 83%, with average annual rainfall of 711.1mm (data from Casement Aerodrome weather station (Met Éireann, 2010)).

Low molecular weight (LMW) PAHs exist in the environment mainly in vapour phases. They volatilise to the atmosphere more readily than HMW PAHs, and can break down over a matter of days to weeks (US Bureau of Environmental Health, 2004). Toxicity increases with increasing molecular weight; the seven potentially carcinogenic PAHs are in the high molecular weight category. Solubility of PAHs is generally low; however the LMW PAHs are more soluble than the HMW PAHs, meaning that they are more mobile in the soil and aquatic environment (ATSDR, 1995a). PAHs can migrate from soils into watercourses during spills/leaks or through urban runoff and infiltration through the soil. Since PAHs are strongly retained by soil organic matter, it is believed that PAH contamination of vegetation including food crops is mainly due to atmospheric deposition and soil splash directly onto vegetation rather than uptake via the roots (UK EA, 2007b).

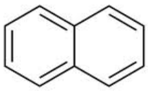
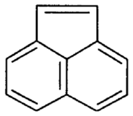
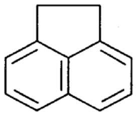
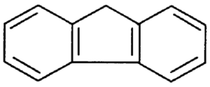
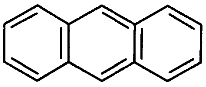
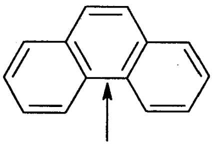
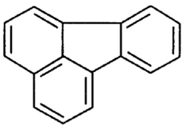
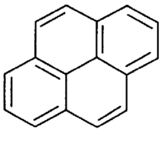
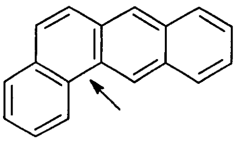
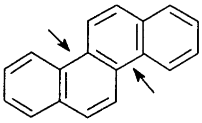
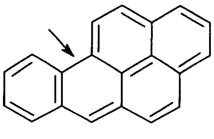
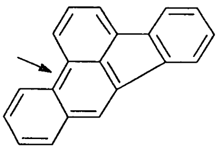
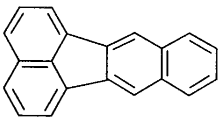
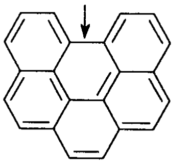
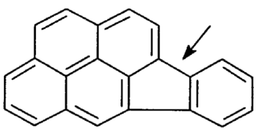
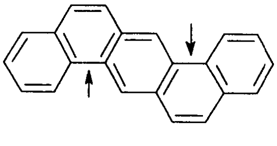
Naphthalene  $C_{10}H_8$ 128 g/mol	Acenapthylene  $C_{12}H_8$ 152 g/mol	Acenaphthene  $C_{12}H_{10}$ 154 g/mol
Fluorene  $C_{13}H_{10}$ 166 mol/g	Anthracene  $C_{14}H_{10}$ 178 mol/g	Phenanthrene  $C_{14}H_{10}$ 178 mol/g
Fluoranthene  $C_{16}H_{10}$ 202 mol/g	Pyrene  $C_{16}H_{10}$ 202 mol/g	Benzo(a)anthracene  $C_{12}H_{12}$ 228 mol/g
Chrysene  $C_{18}H_{12}$ 228 mol/g	Benzo(a)pyrene  $C_{20}H_{12}$ 252 mol/g	Benzo(b)fluoranthene  $C_{20}H_{12}$ 252 mol/g
Benzo(k)fluoranthene  $C_{20}H_{12}$ 252 mol/g	Benzo(g,h,i)perylene  $C_{22}H_{12}$ 276 mol/g	Indeno(1,2,3-c,d)pyrene  $C_{22}H_{12}$ 276 mol/g
Dibenzo(a,h)anthracene  $C_{22}H_{14}$ 278 mol/g		

Table 2 Chemical structure, chemical formulae and molecular weights of PAH compounds (compiled from ATSDR (1995a) and Yunker *et al.* (2002)).

Pyrogenic sources

Pyrogenic PAHs are sourced from the incomplete combustion of organic materials, including fossil fuels and organic waste. During combustion, PAHs are released in vapour and particulate phases. The particulate phase consists of black carbon in the form of fine soot particles and larger char particles to which PAHs adhere. PAHs in urban air predominantly adhere to small-diameter soot particles that have residence times of weeks in the atmosphere and are subject to long-range transport (Butler & Crossley, 1981; cited in ATSDR, 1995a). Large char particles are likely to be deposited near their emission source due to their weight. Pyrogenically-sourced PAH contamination is believed to be characterised by the dominance of HMW PAHs (Banger *et al.,* 2010).

Pyrogenic sources are associated with diffuse pollution mainly from vehicle exhaust emissions, industrial emissions and domestic fossil fuel burning. These sources account for most PAHs in soils (ATSDR, 1995a). Domestic coal burning is a low temperature, uncontrolled and inefficient process compared to industrial coal burning and therefore it emits significantly more PAHs (Wild & Jones, 1995). Industries which can emit PAHs to the environment include power generation facilities, waste incineration sites, hazardous waste sites, metalworks, gasworks and wood-preserving facilities (ATSDR, 1995a). Many historic inner city industries used charcoal, coke or coal as fuel for steam or power generation in the 19th and 20th centuries. At electricity generation facilities PAH contamination may be sourced from storage of raw fuels, disposal of ash and emissions from combustion of fossil fuels (UK DoE, 1995h). Coal carbonisation is associated with PAH contamination through coal combustion emissions to the atmosphere and ground contamination from by-products, coal tar lagoons and coal dust. Historically coal stockpiles were stored directly on the ground and ash was reused as fill on site (UK DoE, 1995a).

Electricity and cleaner fuels such as gas are now used for domestic heating as alternatives to coal but it is expected that a significant loading of PAH contamination was contributed to soils through domestic and municipal power generation in the historic residential core of the city over time. It is expected that the reuse of soil contaminated with coal and its derivatives continues to have an effect on soil quality in Dublin.

Following the eradication of bituminous coal burning in Dublin, road traffic emissions are now the biggest threat to air quality (EPA, 2009a). In many cities the principal source of PM_{10} (respirable atmospheric particulates with diameters less than 10µm) is road traffic emissions, particularly from diesel engines (Jennings *et al.,* 2006). Jennings *et al.* (2006) found during a study of particulate pollution in Dublin between 2001 and 2002 that levels of ambient particulate phase PAHs were highest in Dublin at roadside locations, at concentrations up to 6 times higher than the rural background. Levels were similarly elevated in urban background sites due to diverse urban combustion sources. These findings were consistent with those for other European countries.

The EPA implements an air monitoring network in Ireland and air quality in Dublin is currently described as good according to measurements of particulate matter (EPA, 2009a). A decreasing trend has been observed in PM_{10} concentrations from 2002 to 2008; this is attributed to reduced emissions from progressively cleaner vehicle engines (EPA, 2009a).

Petrogenic sources

Petrogenic PAH pollution sources typically occur through petrochemical spillage or leakage. Petrochemicals are produced from the distillation of crude oil or coal tar and can include various fuel oils (e.g. petrol, diesel, and kerosene), lubricating oil and tars. Creosote is a PAH-rich chemical derived from the distillation of coal tar (a by-product of the carbonisation of bituminous coal). Accidental spillage or leakage of petrochemicals can add a large point source burden of PAH contamination to the soil. If spilled petrochemicals exceed the saturation capacity of soil they may exist as liquid in the soil and in this form can volatilise more readily to air and migrate to water bodies.

Fuel oils contain about 5% PAHs (ATSDR, 1995b). Facilities most commonly associated with fuel oil spills/leaks are petrol stations, garages, scrap yards and fuel storage facilities with underground/overground tank farms, fuel lines and pumps. Industries that are not directly concerned with combustion or the use of petrochemical products can still act as a source of PAH pollution via leaks and spills of oils from fuel storage facilities, machinery and waste materials contaminated with oil.

The composition of creosote varies widely, containing up to 85% PAHs along with phenols and other organic compounds. ATSDR (1995a) gives a typical PAH composition of 21% phenanthrene, 10% fluorene, 9% acenaphthene, 8.5% pyrene, 3% chrysene, 3% naphthalene, 2% anthracene in creosote mixtures. Creosote can contain up to hundreds of parts per million of benzo(a)pyrene, a noted PAH carcinogen (Kohler *et al.,* 2000). It is used as a wood preservative and environmental contamination can result from spills/leaks at wood treatment plants and the leaching of creosote from preserved wood in the environment. Wild and Jones (1995) suggested that creosote treated wood was potentially the largest sink of PAHs in the UK environment. A study of railway sleepers in Switzerland determined that sleepers treated with 5kg of creosote emit the creosote into the environment over a period of 20 to 30 years (Kohler *et al.,* 2000).

Due to its high PAH and other organic chemical content, the marketing and use of creosote has been banned in Ireland since 2003 under the European Communities (Dangerous Substances and Preparations) (Marketing and Use) Regulations 2003 (EPA, 2009b). Exceptions to the regulations include the use of creosote for commercial purposes, including for the treatment of railway sleepers, electricity/telephone poles and agricultural fencing. The regulations specify that creosote treated wood, particularly railway sleepers and wood chippings, may not be used inside buildings, in toys or in parks, recreational facilities or playgrounds. However, wood treated with creosote prior to 2003 may be reused under the regulations and such wood might be unintentionally used in public recreational areas. A study in Japan (Kurata *et al.,* 2005) found that wood chippings made from recycled demolition wood contained creosote as well as heavy metal preservatives (chromated copper arsenate or CCA) and pesticides (DDT and aldrin).

Historical activities which may have imparted PAH contamination to Dublin's soils on a localised basis include those which used coal or oil as a fuel and those which used PAHs as part of industrial processes (e.g. naphthalene and other organic chemicals as tanning agents in tanneries). Such industries were concentrated in the inner city due to the availability of imported coal via Dublin port.

Other minor potential sources of PAHs in the environment include vehicle tyres and tyre-derived products, and cigarette waste. Vehicle tyres can contain sources of petrochemical PAHs. During the tyre production process extender oils containing PAHs can be incorporated into the rubber matrix (FIA, 2008). An amendment to EC Directive 76/769/EEC in 1995 restricted the use and placing on the market of tyres produced with PAH-containing extender oils. It specified that vehicle tyres should be retreaded with low-PAH (less than 10 mg/kg total PAHs) extender oils after 1 January 2010 (FIA, 2008). Since the ban does not apply to tyres manufactured before 2010, older tyres and products derived from recycled tyres may still contain extender oils with PAHs.

People may come into contact with tyre materials in particles of road dust and in playgrounds, where tyres are commonly used in climbing equipment and in anti-fall tyre crumb or tile ground coverings. Although concern has been expressed about exposure of children to chemicals from tyre crumb in playgrounds (Anderson *et al.,* 2006), little research has been carried out on the potential health effects of tyre products in playgrounds. One study concluded that under standard outdoor conditions, there was little potential for tyre crumb to cause adverse health effects in children (Birkholtz *et al.,* 2003). The same study confirmed that chemicals can leach from fresh tyre crumb (in place outdoors for less than 3 months) in quantities toxic to aquatic organisms.

Forty-two percent of all litter in Ireland is composed of cigarette waste (Dept. of the Environment, Heritage and Local Government, 2010). Cigarette butts contain up to 4000 different chemicals, of which 60 are carcinogenic, including PAHs and heavy metals. Discarded cigarette butts are commonly observed in public areas such as at park benches and around dustbins in parks. No studies have been completed to assess localised soil contamination from cigarette waste, but a study showed that chemicals in cigarette butts can leach into the environment when they come into contact with water (Kadir *et al.,* 2009).

Mixed sources of PAHs

In the urban environment PAHs may be sourced from a mixture of pyrogenic and petrogenic sources. Historical landfilling or landscaping with unregulated fill materials is one such activity which may give rise to PAH contamination from a mixture of sources such as soil contaminated with petrochemicals, rubbish, hazardous waste, sewage sludge, ashes and soot. There is anecdotal evidence of such landfilling/landscaping activities having taken place historically in public areas in Dublin.

Bonfires are also associated with possible PAH soil pollution from waste materials, ashes and soot. Historically bonfires were set in public places to mark celebrations throughout the year, typically burning bones, wood and straw. In modern times, bonfires in urban areas burn a variety of modern waste materials as well as wood, causing nuisance and environmental pollution, particularly at Halloween.

A recent study of bonfires and soil contamination in Galway (Dao *et al.,* 2010) found that materials burned at bonfires sites in open space in urban residential areas included tyres, batteries, household white goods, mattresses, furniture and construction materials; causing heavy metal contamination. Burning of such materials has the potential to release organic contaminants such as PAHs from hazardous materials and from the incomplete combustion of organic material. Evidence of such burning was seen in public areas in Dublin as part of the SURGE soil sampling which was carried out around Halloween 2009. Figure 13 shows such a bonfire site, with evidence of burning of domestic rubbish, a mattress and a TV set.

Figure 13 Evidence of bonfire burning in Dublin

4.3.2 Indicators of PAH contaminant source and composition

PAHs normally occur as complex mixtures in the environment. The composition of these mixtures varies according to the contamination source. PAH compositions may be attributed to pyrogenic or petrogenic sources using various techniques. Here the ratios of different PAH compounds are examined to approximate particular contamination sources to soil sample results seen in Dublin.

PAH ratio plots are based on the abundance of PAHs of similar molecular weight, and different ranges of ratios have been established empirically to indicate different contamination sources such as grass/wood/coal combustion, petroleum or petroleum combustion. Yunker *et al.* (2002) critically assessed the use of a number of ratios and determined that the following ratios were most effective in attributing contaminant sources:

- Benzo(a)anthracene to Chrysene (BaA/(BaA+Chry)); where the value of the ratio indicates either petroleum (<0.2), mixed sources (between 0.2 and 0.35) or combustion (>0.35).
- Fluoranthene to pyrene (Fl/(Fl+Pyr)); where the value of the ratio indicates petroleum (<0.4), petroleum combustion (between 0.4 and 0.5) or grass/wood/coal combustion (>0.5).
- Anthracene to phenanthrene (An/(An+Phen)); where the value of the ratio indicates petroleum (<0.1) or combustion (>0.1).

Two ratios may be plotted together on a scatter plot to show visually where soil sample results lie in relation to possible contamination source ranges. These are approximate indications of contaminant source and to obtain more accurate contaminant source attribution, analysis of additional PAH compounds and forensic chemistry techniques would be required.

4.3.3 Polychlorinated Biphenyls

PCBs are man-made organic compounds with 1 to 10 chlorine atoms attached to biphenyl, which is a molecule composed of two benzene rings

(ATSDR, 2000). The generic chemical formula for PCBs is $C_{12}H_{10-x}Cl_x$, indicating that a large number of PCB congeners (compounds) result from the attachment of different numbers of chlorine atoms to the benzene rings (Figure 14) (ATSDR, 2000). PCBs are grouped according to how many chlorine atoms are attached to the biphenyl molecule, e.g. trichlorophenyls are PCB congeners with 3 chlorines. Out of 209 possible congeners, 7 are assessed in this study: PCB Congener Nos. 28 (trichlorophenyl), 52 (tetrachlorophenyl), 101 and 118 (penta-chlorophenyl), 138 and 153 (hexachlorophenyl) and 180 (heptachlorphenyl). Hence increasing congener numbers relate to the increasing degree of chlorination of the PCB compound.

PCBs were first synthesised in the 1930s for industrial uses, as complex mixtures of various compositions. These mixtures were known by a variety of trade names, including Aroclor, Clophen and Fenchlor (ATSDR, 2000). In the 1970s the negative effects of PCBs on human health and the environment were recognised (Section 5.5). The production, marketing and use of PCBs were banned in Europe in 1985 under EC Directive 85/467/EEC. Guidelines for the disposal of PCBs were laid out in 1996 by EC Directive 96/59/EC and these were implemented in the Waste Management (Hazardous Waste) Regulations (1998) in Ireland. The Regulations require holders of PCBs or PCB-contaminated equipment to give notice to the EPA for PCBs and equipment containing more than 5 litres of PCBs every year and to take measures to properly dispose of, label and separate PCB holdings (EPA, 2007).

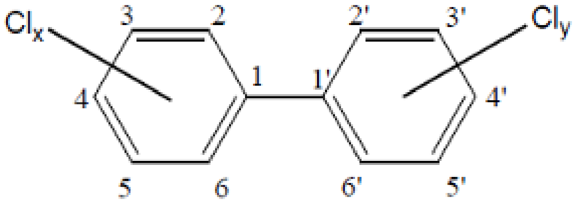


Figure 14 Chemical structure of PCBs (ATSDR, 2000).

4.3.4 Source and fate of PCBs in the environment

Since the restriction of PCB use, concentrations of PCBs in soil have fallen approximately 800-fold in the UK (UK EA, 2007a). However, sources of PCBs remain in the urban environment and concentrations of PCBs in urban soil are still 1.5 times higher than those seen in rural areas (UK EA, 2007a).

PCBs generally persist in soil for years or decades; heavier, more chlorinated PCBs do not readily break down, whereas lighter, less chlorinated PCBs evaporate more readily to the atmosphere (ATSDR, 2000). PCBs can be carried long distances as vapour or adsorbed to solid particles in the atmosphere; as a consequence trace quantities of PCBs are found all over the world (ATSDR, 2000). PCBs have low solubility in water and are highly lipophilic, meaning that they can dissolve and accumulate in fats in human and animal tissue. PCB uptake into plants via roots is negligible; PCB concentrations in plants mainly reflect those from atmospheric deposition (UK EA, 2007c). It was estimated in 1994 that the bulk of the environmental PCB burden was held in soils (93%), with the rest in seawater (3.5%); marine sediments (2%); freshwater sediments, vegetation, humans and sewage sludge (1%); and air and freshwater (<1%) (Harrad *et al.,* 1994).

Due to their chemical stability, PCBs were commonly used as dielectric and coolant fluids in electrical equipment such as transformers and capacitors and as additives to paint, plaster, dyes and flame retardants (ATSDR, 2000). Their use is normally categorised into closed applications (electrical equipment) and open applications (paints etc).

Closed PCB applications

Closed PCB applications are those in which PCBs are contained within electrical equipment as components of oils used as dielectric fluid, heat exchange fluid, hydraulic fluid and lubricating oils. Electrical equipment which may contain PCBs include electrical transformers, capacitors, lighting ballasts and circuit breakers, especially those manufactured up to and including the 1980s (EPA, 2007). PCBs were commonly used in such applications due to their chemical stability and excellent electrical insulation and heat transfer properties (EPA, 2007). Power stations built between 1940 and the 1980s may have used PCB-containing transformers and capacitors; although their use has been phased out, PCB contamination of soils may have occurred during spills, retrofitting or decommissioning of plants (UK DoE, 1995h).

Closed applications can result in relatively high concentrations of PCBs in the environment when spills or leaks occur from PCB-containing equipment at sites where they are used, or when waste electrical equipment is improperly disposed of in landfills or elsewhere (Robertson and Hansen, 2001). Fires involving electrical equipment containing PCBs can greatly increase the toxicity of PCBs through the formation of chlorodibenzofurans and other organic chemicals (ATSDR, 2000).

Open PCB applications

Open PCB applications are those in which PCBs are used as an additive, such as in paints, dyes, inks, adhesives, flame retardants, pesticides, plaster and mortar (ATSDR, 2000 and Jartun *et al.,* 2009). These sources can result in widespread, low-level diffuse releases to the environment over a long time (Robertson and Hansen, 2001).

High levels of PCBs (8-9% by composition) have been found in old paint (from 1950s – 1970s) used on building exteriors, interiors, ships and bridges (Jartun *et al.,* 2009 and studies cited therein). Weathering of painted surfaces can lead to increased levels of PCBs in the urban and marine environments. Weathering mechanisms causing flaking/chipping of old painted surfaces include exposure to heavy rainfall and wind, sandblasting and powerwashing (Jartun *et al.,* 2009). PCBs in paint flakes can be mobilised into local soils, into the atmosphere or into urban runoff systems and subsequently into aquatic environments. Jartun *et al.* (2009) highlighted the importance of understanding the PCB composition of building materials prior to renovation or demolition, to avoid release of PCBs into the environment.

4.3.5 Indicators of PCB contaminant source and composition

Identification of the source of PCB contamination is difficult due to the varying compositions of PCB mixtures and the complexity of transport and degradation processes in the environment, which can change original PCB compositions (Cachada *et al.*, 2009). However, PCB compositions in collected soil samples may be compared to typical compositions found in commercial PCB mixtures (Section 6.3).

Specific PCB mixtures of Aroclor 1254 and 1260 were commonly used in European paints (Cachada *et al.*, 2009) and transformers (ATSDR, 2000). The last two digits in the product name refer to the percentage of chlorine in the mixture, i.e. 54% for Aroclor 1254. Their high chlorine content is attributed to a composition dominated by highly chlorinated PCBs. Aroclor 1254 is associated with pentachlorophenyl PCBs (PCB congeners 101 and 118) and Aroclor 1260 with hexachlorophenyl PCBs (Congener nos. 138 and 153). Heptachlorophenyl PCBs (Congener no. 180) are associated with both Aroclor mixtures (Cachada *et al.*, 2009).

5 Soil Geochemistry and Human Health

5.1 Introduction

People may be exposed to contaminants in soil through three main exposure pathways:

- **Inhalation** of vapours, dusts and particles containing contaminants;
- **Ingestion** of dusts and particles containing contaminants; eating food that was grown in contaminated soil and drinking contaminated water;
- **Dermal (skin) contact** with contaminated soil.

Exposure to contaminants in soil may occur through gardening; children playing in the garden and eating soil; eating home-grown fruit and vegetables or coming into contact with soil or dust which has been brought indoors on shoes and clothes.

Factors to consider when assessing exposure include (Jeffries and Martin, 2009):

- Frequency of exposure or the number of days per year in which an exposure event occurs;
- The age of the human receptor;
- The concentration of contaminant taken in and processed by the body;
- The exposure duration or the average daily chemical intake/uptake.

Bioavailability is an important consideration which relates to how the human body takes up contaminants. Some contaminants may pass through the human body with relatively little effect while others may be taken up by multiple human organs and systems, depending on the nature of the human receptor, the chemical contaminant and the exposure route.

5.2 Heavy metals

People are exposed to small amounts of heavy metals which naturally occur in food and water. Many metals are essential in small quantities for life but they are toxic in large quantities (Alloway, 1995). The heavy metals which tend to give rise to most concern with regard to human health are Pb, Hg, As, Cd, Ni, Zn, Cr, Cu, Be, Co. The use of Pb, Hg, As, Cd and Ni in consumer products is restricted in the EU under the REACH directive (Commission of the EC, 2007), which aims to protect human health from hazardous substances.

Different metals have different effects on the human body. Health effects for the main metals of human health concern are described in the results section. Exposure to normal levels of other trace metals is not usually harmful, but exposure to high levels can affect human health. Exposure to high levels of these trace metals is usually only associated with working in or living near industries which use, or have used, large amounts of metals.

5.3 Persistent Organic Pollutants

POPs can persist and accumulate in the environment and in the human body, where they can cause adverse effects to the environment and to human health. PAHs and PCBs are lipophilic, meaning that they dissolve and accumulate in fatty tissues in the human body (ATSDR, 1995a and 2000). When PAHs and PCBs enter the human body they can be changed into harmful metabolites and may remain in the body for months to years (ATSDR, 1995a and 2000).

Estimating human exposure to both PCBs and PAHs is difficult due to their occurrence as complex mixtures and the presence of other chemicals in such mixtures (ATSDR, 1995a & 2000).

5.4 PAHs

Most PAH exposure to the population is from cigarette smoking, domestic fire smoke and occupational exposure in workplaces which use PAHs (ATSDR, 1995a). PAHs are known to cause adverse human health effects (e.g. bronchitis, dermatitis) (NIOSH, 2005) and seven PAH compounds are classed as known animal carcinogens and probable human carcinogens targeting the lungs, kidneys and skin:

- Benzo(a)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Chrysene
- Dibenz(a,h)anthracene
- Indeno(1,2,3-c,d)pyrene.

5.5 PCBs

Human exposure to PCBs occurs mainly through low-level food contamination (especially in fish, meat and dairy) and historically through occupational exposure (ATSDR, 2000). Most studies relating to the effects of PCBs on human health relate to occupational exposure and have documented damage to skin, nose, eyes, gastrointestinal tract, blood and liver as possible reactions to PCB exposure (ATSDR, 2000). Based on evidence from animal testing, PCBs are classed as potential human endocrine disruptors and potential human carcinogens. Endocrine disruptors mimic or block hormones in the human body, causing interference with the reproductive, immune and neurobehavioral functions (ATSDR, 2000).

A public health alert resulted in Ireland in December 2008 when pork products were found to have elevated PCB levels as a result of contaminated animal feed. The Food Safety Authority of Ireland ordered the recall of pork products after pig meat was found to have levels of PCBs above the recognised safety limit for PCBs in food (FSA, 2009).

5.6 Risk assessment

In Ireland there is no dedicated contaminated land guidance which advises on the assessment of soil contamination in relation to human health and the environment. The EPA supports the application of the U.K. Contaminated Land Exposure Assessment (CLEA) approach in Rep. of Ireland in the absence of a dedicated Irish regime. CLEA produces guidelines for human health risk assessment of contaminated land and provides levels of soil contamination below which risks to human health are considered minimal, known as Soil Guideline Values (SGVs) (Jeffries & Martin, 2009).

The CLEA approach is based on the source-pathway-receptor model for assessing risk to human health. A source of contamination, an exposure pathway and a human receptor must be established before a significant risk to human health can be confirmed, i.e. there must be a pollutant linkage. In this regard a source of contamination does not necessarily pose a risk to human health if there is no exposure pathway or human receptor present. This concept is applied in the CLEA methodology by taking into account the intended land use of a site under assessment. Land use can determine pollutant linkages at a site, e.g. there are potentially more exposure pathways and human receptors associated with contaminated soil under residential land use than commercial land use. The generic land use scenarios are described as follows (Jeffries & Martin, 2009).

- Residential: a domestic dwelling with private garden including a vegetable patch.
- Allotment: a plot of open space used for growing fruit and vegetables for domestic consumption.
- Commercial: property consisting of a building at which employees work.

Each scenario has generic assumptions about critical receptors, exposure times and exposure pathways.

5.6.1 UK CLEA Soil Guideline Values

SGVs represent levels that when exceeded may pose a possibility of significant harm to human health. An exceedance of an SGV indicates the need for further site investigation in order to refine the risk assessment. If further investigations determine that a significant risk to human health is likely, measures must be taken to reduce the risk. Such measures can include the protecting the receptor (e.g. restrictions on site use, for instance vegetable growing), blocking the pollutant pathway (e.g. soil sealing or capping) or removal of the contaminant source (e.g. soil removal or remediation). The CLEA risk assessment model derives SGVs by comparing human exposure to Health Guideline Values that represent a minimal risk to human health from chronic exposure. Human exposure is calculated using a generic site conceptual model, contaminant fate and transport, and long-term human behaviour at the site.

CLEA has recently revised its approach to SGV determination and has withdrawn previous SGVs. SGVs reflecting the new approach are available for some metals (As, Ni, Hg, Se and Cd) and organic compounds (benzene, toluene, ethylbenzene, xylene (BTEX); dioxins, furans and phenol). Available SGVs for metals measured in this study are given in Table 3. No SGVs are currently available for Pb or PAHs. SGVs are available for dioxin-like PCBs when summed with dioxins and furans, and as such are not applicable to this study. In the absence of appropriate SGVs, the CLEA methodology recommends deriving customised Site-Specific Assessment Criteria for particular sites with the CLEA software, using site specific information.

		mg/kg		
		Residential	**Allotment**	**Commercial/ industrial**
As		32	43	640
Cd		10	1.8	230
Hg	Elemental	1	26	26
	Inorganic	170	80	3,600
	Methyl	11	8	410
Ni		130	230	1,800

Table 3 UK CLEA Soil Guideline Values for selected metals (compiled from UK EA (2009a, 2009b, 2009c, 2009d))

Deriving site specific inputs requires detailed site investigation which aims to characterise the sources, pathways and receptors of contamination at a site. Site investigations typically require a desk study and fieldwork to understand the following site characteristics:

- The historical, geographical and geological setting of the site;

- The type, extent and age of contamination present;
- Site conditions which may lead to human exposure such as soil type, vegetation cover, etc; and
- How users of a site may potentially be affected, based on the land use and the type of activities occurring at the site.

5.6.2 Using SGVs in Ireland

There are no CLEA SGVs available for PAHs and PCBs to compare to results measured in the Dublin SURGE Project. Most sites sampled as part of the Dublin SURGE Project are characterised by only one soil sample and limited visual observations of site characteristics. This information is not sufficient to gain an accurate understanding of contaminant sources, pathways and receptors required to derive Site Specific Assessment Criteria and assess potential risk to human health at a site.

Defining human health criteria for contaminants in soils is founded on ecotoxicological studies and usually takes into account the regional geochemical baseline. This means that defining a human health criterion for a region takes into account the typical range of conditions in that region. Accordingly, health criteria are strictly only for application in the geographic region for which they are derived.

Experience from the UK, and other regions such as the Netherlands and Norway shows that establishment of authoritative contaminated land guidance relies on the close cooperation of health authorities, regulators and environmental experts. It is recommended that a contaminated land guidance and regulatory regime be put in place for Ireland in order to prevent deterioration of Ireland’s soil resource and to protect human health from soil contamination, especially in urban areas. It is recommended that an interagency taskforce be set up to further this objective. The Dublin SURGE Project baseline data could form a basis for this work but it is outside the scope of the project to establish SGVs or other means of assessing risks to human health from individual sites.

6 Results

In this section the baseline levels of inorganic elements and persistent organic compounds is described for the greater Dublin area without reference to individual sites.

6.1 Inorganic elements results

In this section results for inorganic elements are presented. Heavy metals which are known to pose a risk to human health are described in detail: As, Be, Cd, Co, Cu, Hg, Ni, Pb, V and Zn. Most of these metals are anthropogenic heavy metals, i.e. they are associated with contamination due to human activity. Geogenic metals, or metals which naturally occur in soils, and inorganic elements are described briefly. Geogenic metals are in general are thought to pose less of a risk to human health because the metals are bound in the soil matrix and are therefore unlikely to be taken up in the human body.

Basic statistics for all inorganic elements measured are shown in Table 4. Results are expressed as mg/kg dry weight of soil except in the cases of Al, Ca, Fe, K and Mg where due to their abundance in soils they are expressed as a percentage of the dry weight of soil. 1% content of an element in dry weight of soil is equivalent to 10,000 mg/kg of that element in dry weight of soil.

	MDL	No. <MDL	% <MDL	Min.	Max.	Mean	Median	Standard deviation
Al	0.003%	0	0	0.14%	5.55%	3.00%	2.88%	0.63%
As	3	4	0.4	<3	402	15.5	13.4	15.2
B	15	25	2.4	<15	99	33.1	34	9.26
Ba	1.5	0	0	24.5	3740	197	175	162
Be	0.15	0	0	0.16	11.3	1.42	1.35	0.54
Ca	0.015%	0	0	0.09%	34.6%	4.34%	3.73%	3.31%
Cd	0.15	3	0.3	<0.15	10.5	1.77	1.74	0.66
Ce	3	0	0	4.00	55.8	31.3	31.9	5.56
Co	0.15	0	0	0.39	24.8	9.8	9.58	2.54
Cr	0.3	0	0	4.24	262	44.2	44.3	11.8
Cu	1.5	1	0.1	<1.5	6,480	50.7	35	203
Fe	0.00045%	0	0	0.31%	5.48%	2.12%	2.21%	0.45%
Hg	0.0075	0	0	0.0135	23.9	0.339	0.206	0.825
K	0.015%	0	0	0.06%	1.71%	0.73%	0.74%	0.18%
La	0.15	0	0	2.43	29.2	17.4	17.8	3.06
Li	0.75	0	0	2.34	128	30.1	28.4	11.1
Mg	0.015%	0	0	0.07%	12%	0.48%	0.43%	0.39%
Mn	7.5	0	0	89.4	5,640	1,040	946	506
Mo	1.5	508	48	<1.5	14	1.46	1.5	0.90
Na	300	7	0.7	<300	2,460	671	657	156
Ni	1.5	0	0	5.5	145	40.7	41	10.9
P	15	0	0	165	5,060	1,174	1,040	510
Pb	3	1	0.1	<3	3,120	123	73.7	192
Sc	0.15	0	0	0.18	11.8	6.00	6.12	1.33
Si	375	159	15	<375	1,560	573	570	237
Sr	1.5	0	0	11.9	1,330	139	127	78.2
Ti	1.5	0	0	20.8	575	208	201	55.0
V	1.5	0	0	10.8	114	70.4	72.1	14.7
Y	0.15	0	0	2.36	26.4	14.6	14.9	3.22
Zn	3	0	0	18	8,390	248	172	373
Zr	3	4	0.4	<3	21.1	12.7	12.9	2.57

Table 4 Basic statistics for 31 inorganic elements, in mg/kg unless otherwise indicated.

6.1.1 Arsenic - As

Arsenic is a grey-coloured amorphous or brittle metalloid (ATSDR, 2007b). It occurs primarily in the mineral arsenopyrite (FeAsS) but is associated with many mineral occurrences (O'Neill, 1990), particularly Cu, Pb, Au and Ag ores. Most As is produced as a by-product of the extraction of these deposits (O'Neill, 1990).

Arsenic compounds were widely used in the past in pesticide products. Now about 90% of all As is produced for use in copper chromated arsenate (CCA) wood preservatives (ATSDR, 2007b). The use of arsenic compounds for wood preservation or pest control is now being phased out under EU Directive 2006/139/EC and is restricted to professional and industrial use (Commission of the EC, 2006a) due to the toxicity of As.

Human activities which contribute most As into the environment are metal smelting, which represents 40% of the anthropogenic total, followed by coal burning (20%) (ATSDR, 2007b). Coal can contain up to 200 mg/kg As and coal ash can have a wide range of As contents (300-700 mg/kg), depending on the composition of source coals (Wedepohl, 1983). Arsenic is chemically similar to P and phosphate fertilisers are another potential source of As (ATSDR, 2007b).

Basic statistics and spatial distribution

As concentrations were determined using ICP-AES, with a method detection limit of 1.5 mg/kg. Arsenic was detected at levels ranging from below the limit of detection to 402 mg/kg, with a median value of 12.7 mg/kg in the greater Dublin area. Results for 0.3% of the samples were below the limit of detection for As.

The spatial distribution of As in the greater Dublin area (Figure 16) is influenced both by human activity and regional geology. Enrichments of As occur in the city centre associated with human activity, and in rural areas associated with localised bedrock mineralisation and mining activities. Anthropogenic activities which are likely to have contributed As to the inner city environment include coal burning, industry and CCA-treated wood.

When As concentrations in the study area are examined by bedrock type (Figure 15), samples taken on the Cambrian greywackes, sandstones, mudstones and quartzites of Howth Head and the Silurian sandstones, greywackes and shales of southwest Co. Dublin have the highest median concentrations of samples taken on different rock types, with 22.4 mg/kg and 24.7 mg/kg As respectively. Argillaceous (clayey) rocks such as shales, mudstones and slates have significantly higher As levels (up to 900 mg/kg) than other rock types (O'Neill, 1990). Arsenic tends to be found associated with sulphide-bearing minerals, which leads to elevated levels in soils in many mineralised areas (O'Neill, 1990). Arsenopyrite (FeAsS) is a sulphide mineral which is present in the metasediments of southwest Dublin and Howth Head. This is likely to account for the naturally elevated levels of As observed in these areas.

In the central southern and southeastern region of the study area, bedrock mineralisation occurred in association with the Leinster Granite intrusion. Heat from the granite caused older surrounding sedimentary rocks to recrystallise into schists and caused metals in the rocks to be concentrated into mineral veins (O'Connell, 1994). In the Tallaght/Bohernabreena hills area, a swarm of volcanic dolerite dykes intrude into the surrounding country rock. These intrusions acted as a conduit for hydrothermal fluids which caused localised metallic mineralisation.

Arsenic is also associated with Pb-bearing ores and As contamination may have occurred in areas where Pb was mined and processed, such as at Ballycorus in the southeast of the study area.

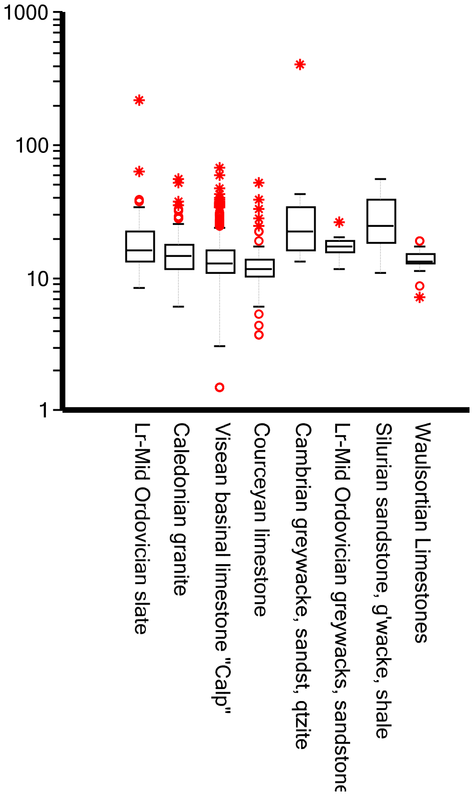


Figure 15 Aresenic boxplots by bedrock type

Several other As anomalies are evident in the study area, at Huntstown, Malahide and Dún Laoghaire. There are minor Pb workings in the Huntstown and Malahide vicinities, which may be associated with As mineralisation. A combination of nearby Pb mineral localities and urban activities at Malahide and Dún Laoghaire could account for the enriched levels of As seen in those areas.

Baseline

The spatial distribution of As indicates areas of both anthropogenic and geogenic influences on soil As. This observation is supported by the CP curve which shows a break between natural and anthropogenic near the centre of the line at approximately 20 mg/kg. This upper limit for the arsenic baseline is within the levels in measured in NSDB rural Dublin soils, which range between 10.1 mg/kg and 27.1 mg/kg. Levels above 20 mg/kg relate to natural As anomalies or anthropogenic contamination.

Human health

Of many possible As compounds, inorganic As compounds pose the most risks to human health (ATSDR, 2007b). This section is concerned with inorganic As only.

The toxicity of As to humans is well known, having been used historically as a poison. Most modern exposure of the human population to As is through small amounts in food, particularly seafood, and contact with soil and CCA wood (ATSDR, 2007b). When ingested and inhaled into the body, As is generally excreted within weeks or months (ATSDR, 2007b). Arsenic is a confirmed human carcinogen and longterm exposure is associated with cancer of the skin, liver, bladder and lungs (ATSDR, 2007b).

The UK CLEA guidance gives SGVs for As in residential, allotment and commercial land uses (Table 5). It is beyond the scope of this study to make assessments of the risk to human health from As concentrations on individual sites in the absence of detailed site-specific information. However, the results are compared to the UK SGVs to give an overview of soil quality in Dublin in relation to As. Thirty four samples exceed the

SGV for residential use. These samples constitute 3% of all samples taken and include samples both in inner city and rural areas. Of these, 11 also exceed the SGV for allotments. None of the results exceeds the SGV for commercial land use. Most of the exceedances occur as isolated single samples, however, hotspots of multiple exceedances occur at Howth Head, southwest Co. Dublin and southeast Co. Dublin near Ballycorus.

Land use	UK CLEA SGV for As (mg/kg)	No. of exceedances
Residential	32	34
Allotment	43	11
Commercial	640	None

Table 5 UK CLEA human health criteria for As

It must be noted that the bioavailability of As varies between anthropogenic and geogenic arsenic. Some forms of naturally occurring contaminants may be tightly bound within the soil matrix and pass through the human body without being released and taken up by the body (UK EA, 2009a). It is possible that the naturally elevated As levels seen along the margins of the Leinster granite and at Howth Head are less bioaccessible, and therefore potentially pose less risk to human health, than As concentrations in areas influenced by human activity (inner city and mining areas). However, adverse human health effects relating to drinking groundwater with high natural levels of As have been reported in over 20 cases worldwide (Mukherjee *et al.,* 2006.) Naturally elevated topsoil As concentrations can indicate areas where groundwater is also enriched with As. From this perspective the issue of As should be addressed for drinking water supplies derived from areas in which geological materials are naturally enriched with As, such as in southwest Dublin. It is recommended that where the provenance of As in soil or groundwater is not well understood, testing for speciated As compounds should be undertaken, in particular with regard to inorganic As compounds.

In the UK, where areas of naturally elevated arsenic are present, *in vitro* biaccessibility tests are used to determine the approximate proportion of soil As which would be available for uptake by the human body if exposed (UK EA, 2009a). These tests simulate the biochemical conditions of the gastrointestinal system to extract bioaccessible As from soil samples. UK CLEA states that bioaccessibility testing carried out according to current best practice may contribute to a greater understanding of the risk of arsenic to human health on a site-specific basis (UK EA, 2009a).

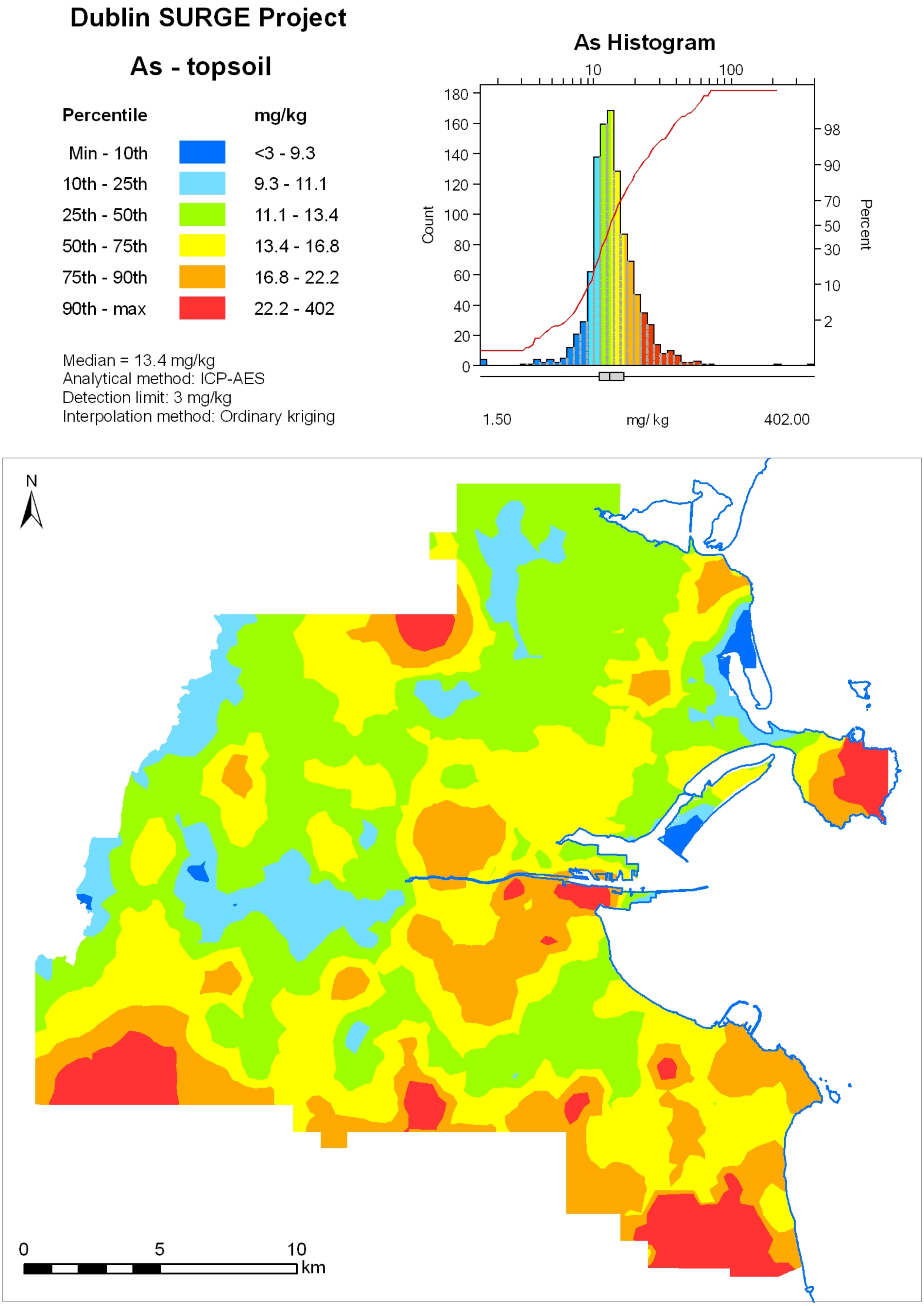


Figure 16 Topsoil As concentrations in the greater Dublin area

6.1.2 Beryllium – Be

Pure Be is a hard greyish metal (ATSDR, 2002). Beryllium is the lightest metal and it occurs mainly in granite pegmatite rocks as the mineral beryl (Wedepohl, 1983; ATSDR, 2002). Beryllium concentrations are generally low in sedimentary rocks, but it is known to accumulate in coals and coal ash (Wedepohl, 1983).

Most Be is used to make alloys for precision instruments and electrical/electronic parts used in vehicles, computers, sports equipment and military applications (ATSDR, 2002). The most significant human activity which causes Be contamination in the environment is coal burning (UK EA, 2010a). Other sources may include chemical manufacturing and metal alloying facilities that use Be.

Basic statistics and spatial distribution

Beryllium concentrations were determined using ICP-AES, with a method detection limit of 0.15 mg/kg. Be was detected at levels ranging from 0.16 mg/kg to 11.3 mg/kg, with a median value of 1.35 mg/kg.

The spatial distribution of Be in the greater Dublin area (Figure 18) is influenced by both regional geology and human activities, particularly in the port area. In the southeast Dublin an area of natural Be enrichment in topsoils is evident in association with the Leinster Granites. The median concentration of Be in topsoils overlying granite is higher than the other bedrock types at 1.6 mg/kg (Figure 17). Samples taken on the granite till subsoil type also had a higher median Be concentration (1.64 mg/kg) than samples taken on other subsoil types.

There are several varieties of granites in the Leinster intrusion, some of which host naturally high levels of Be. Muscovite-enriched granites occur around the Sandyford, Stepaside and Kiltiernan areas in the southeast of the study area. The Be contents of muscovites can be appreciable, ranging from 10 to 50 mg/kg (Wedepohl, 1983). Beryllium is also associated with aplite, an igneous intrusive rock which cuts across the granite and occurs at the margins of the granitic pluton. GSI records indicate a beryl mineral location at a granite quarry in Glencullen, located some 2km outside the southern boundary of the study area.

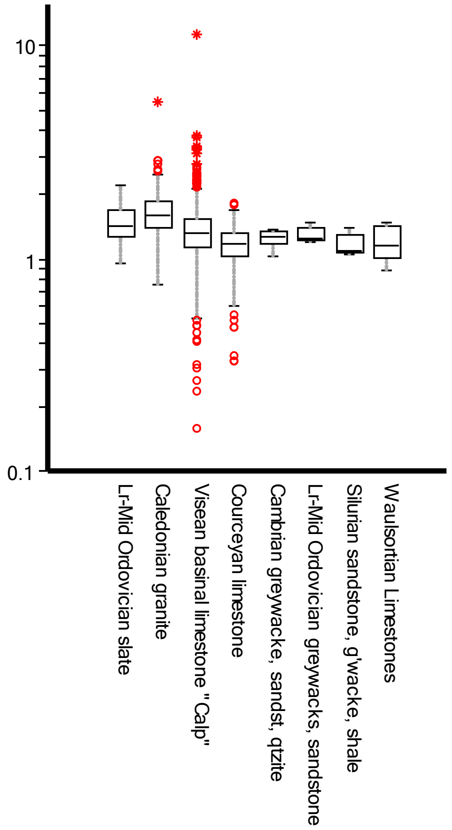


Figure 17 Boxplots of Be by bedrock type

An area of Be enrichment is also evident in topsoils overlying limestones in band stretching from Cabra towards the boundary with the Leinster Granites in Dundrum. Wedepohl (1983) states that the Be content of sedimentary rocks is generally low, although higher Be contents may be observed in association with the presence of clayey minerals. Be concentrations in this area may be related to high clay contents of impure limestones in the Dublin Basin.

Beryllium concentrations are elevated (above the 90th percentile concentration for Be) in the heavy industry zone in the Dublin port area. Since soils in this area are composed of made ground, it is likely that Be levels observed are due to anthropogenic contamination. Possible sources of anthropogenic Be in made ground in the docklands area include coal and oil burning, coal storage, coal fly ash disposal and industrial activity.

Baseline

The spatial distribution of Be indicates areas of both anthropogenic and geogenic influences on soil As. This observation is supported by the CP curve which shows a break between natural and anthropogenic near the centre of the line at approximately 1.8 mg/kg. This upper limit for the Be baseline is within the levels in measured in NSDB rural Dublin soils, which range between 1.15 mg/kg and 2.93 mg/kg. Levels above 1.8 mg/kg relate to natural Be anomalies or anthropogenic contamination.

Human health

Exposure to high levels of Be usually occurs in association with industries which process Be or hazardous waste sites (ATSDR, 2002). Health effects associated with inhaling high levels of Be dust include lung disease and lung cancer (ATSDR, 2002). The general public is not likely to be exposed to such high levels of Be (ATSDR, 2002). Most Be in soil does not dissolve in water and remains bound to the soil. However, some water-soluble forms of Be pose a greater risk to human health than insoluble forms. In general Be does not accumulate in the food chain.

There is currently no UK CLEA SGV available for assessing risks to human health from soil Be concentrations.

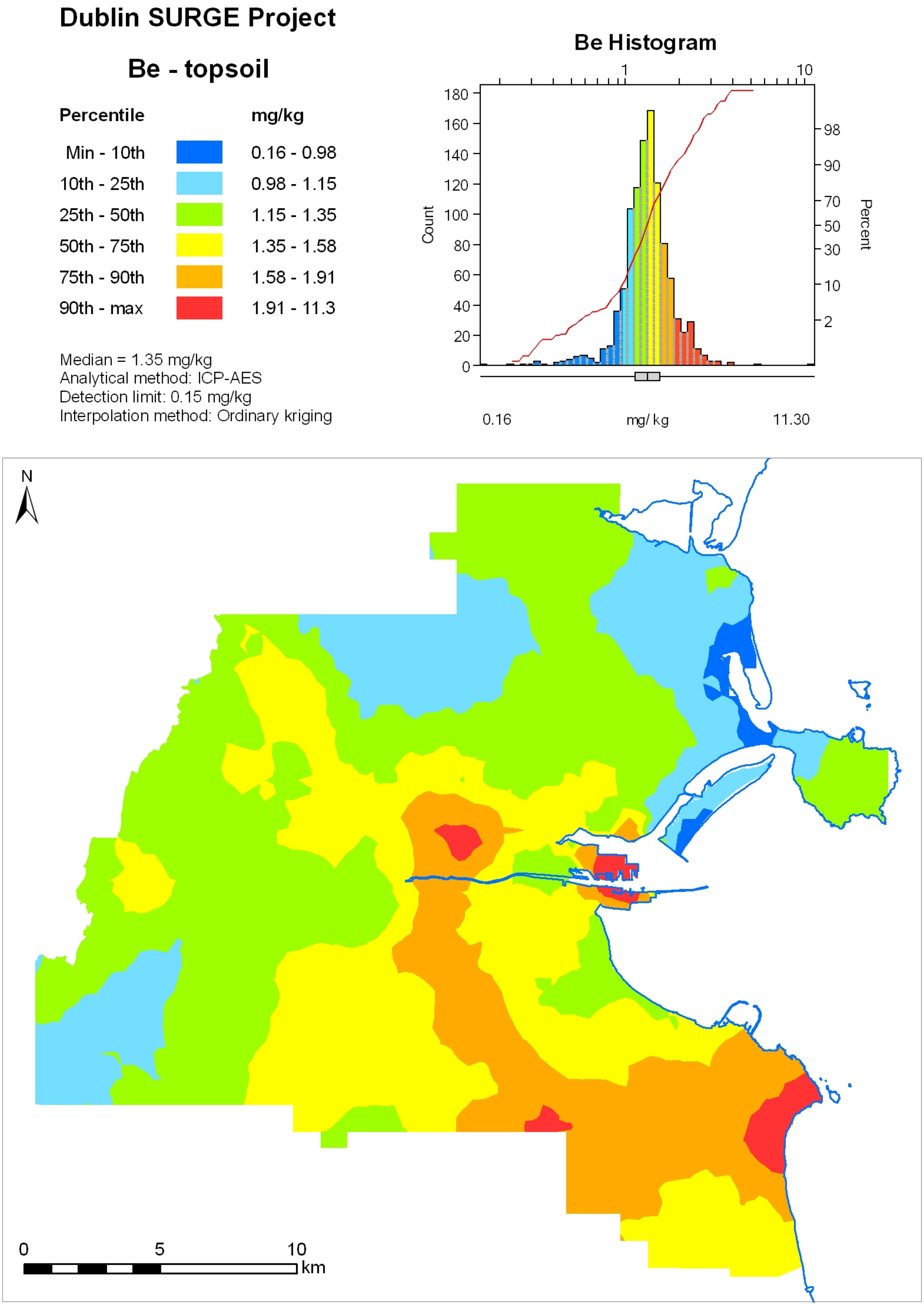


Figure 18 Topsoil Be concentrations in the greater Dublin area

6.1.3 Cadmium – Cd

Pure Cd is a soft, silver-white lustrous metal (UK EA, 2009b). Cadmium is a relatively rare metal and concentrations in uncontaminated soils are usually low (Alloway, 1990). Cadmium compounds occur mainly in association with Zn ores and these are the primary source of Cd worldwide (UK EA, 2009b). Unlike Pb, Hg and Cu which have been used in human activities for centuries, most Cd has been used and produced since the 20th century (Alloway, 1990). Over 80% of Cd is used in batteries, with the rest used in metal plating and alloys; pigments, tyres and lubricating oils and as stabilisers in plastics (ATSDR, 2008a; Alloway, 1990). Cadmium also occurs in phosphate fertilisers and in sewage sludge, both of which can contribute Cd to soils when spread on land.

Human activities which can cause Cd contamination include Zn mining and smelting, incineration of wastes containing Cd, application of phosphate fertilisers, and the burning of fossil fuels (ATSDR, 2008a; Alloway, 2005). European coals and fly ash contain Cd amongst other trace elements (Fuge, 2005).

Basic statistics and spatial distribution

Cadmium concentrations were determined using ICP-AES, with a method detection limit of 0.075 mg/kg. Cadmium was detected at levels ranging from below the limit of detection to 10.5 mg/kg, with a median value of 1.65 mg/kg in the greater Dublin area. Results for 0.3% of the samples were below the limit of detection for Cd. Cadmium levels in rural soils in the greater Dublin area as measured in retested NSDB samples range between 0.58 mg/kg and 2.09 mg/kg.

The spatial distribution of Cd in the greater Dublin area (Figure 19) is strongly influenced by regional geology, with possible influences from human activities in the inner city. The Soil Geochemical Atlas of Ireland notes natural enrichments (ranging from 1-15 mg/kg) of Cd in an area encompassing counties Westmeath, Meath, Kildare and Dublin, which are attributed to naturally high Cd levels in impure limestones. This Cd-enriched band stretching from the midlands to Dublin is evident in the west of the study area, where concentrations exceeding the 90th percentile concentration for Cd are extensive. Bedrock in this area consists of dark grey impure limestones and shales, known as the Lucan Formation or Calp. This formation extends west and northwest into the midlands where it hosts a world-class Zn and Pb deposit in Co. Meath, which is mined at Tara Mines, near Navan. It is likely that bedrock in the study area is naturally enriched with Cd, particularly in the east, due to its strong affinity with Zn.

Apart from extensive areas of enriched Cd in the west of the study area, levels of Cd are variable, with no strong patterns evident in relation to bedrock type, land zone, location type, subsoil type or proximity to the city centre. Median concentrations in the limestones are slightly higher than other bedrock types at around 1.8 mg/kg. Median concentrations of Cd in samples taken in industrial land zones are slightly higher than other land zones at 1.9 mg/kg.

Baseline

The spatial distribution of Cd indicates that soil Cd is mainly determined by regional geology, with influences from anthropogenic activity in inner city industrial areas. This CP curve shows a break between natural and anthropogenic concentrations at approximately 3 mg/kg. Cadmium levels in rural NSDB soils in the Dublin area range between 0.6 mg/kg and 2.1 mg/kg.

Human health

Cadmium has no essential biological functions and is toxic to plants and animals (Alloway, 1990). The main routes of exposure of the general population to Cd is through food consumption (especially shellfish and organ meat) and smoking (ATSDR, 2008a). People who live near, or work in Cd-emitting industries may be exposed to higher levels of Cd.

Longterm exposure causes Cd to build up in the liver and kidneys, where it can remain for many years and affect liver and kidney function (ATSDR, 2008a). Cadmium is considered a human carcinogen. The inhalation of particles containing Cd is associated with lung cancer (ATSDR, 2008).

The UK CLEA guidance gives SGVs for Cd in residential, allotment and commercial land uses. Table 6 shows the SGVs for Cd and gives the number of SURGE results which exceed these levels. It is beyond the scope of this study to make assessments of the risk to human health from Cd concentrations on individual sites in the absence of detailed site-specific information. However, the results are compared to the UK SGVs to give an overview of soil quality in Dublin in relation to Cd. One sample of 10.5 mg/kg Cd exceeds the SGV for residential land use (10 mg/kg). This exceedance occurs near the eastern margin of the Leinster Granites, in an area of known bedrock Pb-Zn mineralisation. 487 samples exceed the SGV for allotment use (1.8 mg/kg) in the study area. Consumption of homegrown produce is the most significant exposure pathway for allotment and residential land uses. Although Cd uptake by plants varies widely, lettuce, spinach, celery and cabbage are reported to accumulate Cd (UK EA, 2009b).

Land use	SGV for Cd (mg/kg)	No. of exceedances
Residential	10	1
Allotment	1.8	487
Commercial	230	None

Table 6 UK CLEA human health criteria for Cd

The SGV for allotments is stringent because it is based on a soil concentration that gives rise to Cd levels in plants that are below the maximum permissible levels allowed in food commercially sold on the market (UK EA, 2009b). It may be overly stringent for the Irish situation considering the naturally high Cd levels seen in topsoil derived from limestones in the Dublin basin. Geogenic Cd is likely to be less bioavailable to plants and humans than Cd associated with contamination from industry or mining (UK EA, 2009a). Also, homegrown produce is likely to contribute only a small fraction of the diets of typical householders. Where the SGV is exceeded, UK CLEA guidance states that collecting data on soil pH and organic matter content may refine understanding of Cd availability to plants on a site specific basis.

None of the results exceeds the SGV for commercial land use.

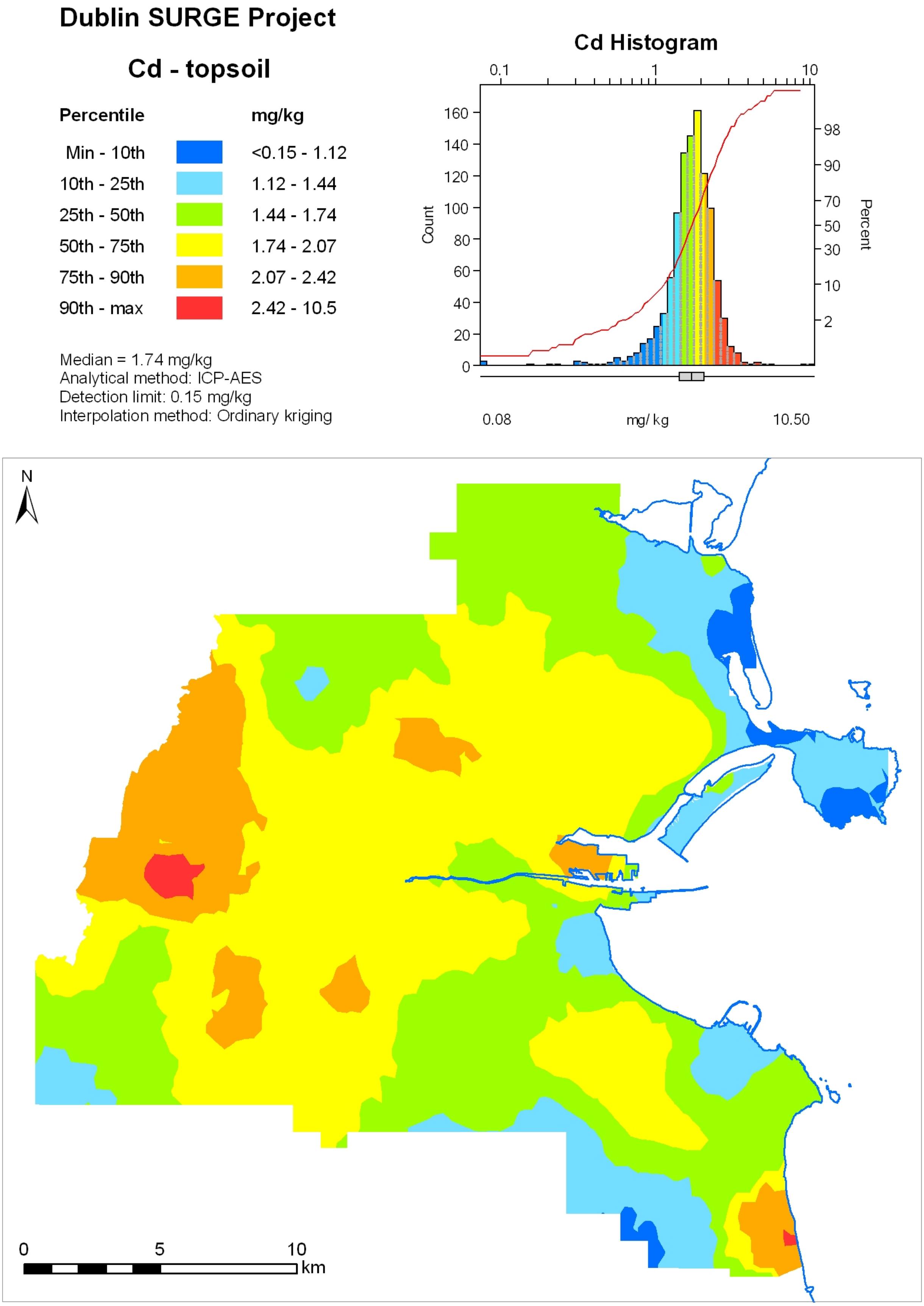


Figure 19 Topsoil Cd concentrations in the greater Dublin area

6.1.4 Cobalt - Co

Pure Co is a hard silvery grey metal (ATSDR, 2004b). Co is abundant in basaltic igneous rocks and is generally depleted in limestones but tends to vary with Fe and Mg contents (de Vos and Tarvainen, 2006).

Cobalt is used to make alloys for industrial and military applications and as blue colorants in glass, ceramics and paints (ATSDR, 2004b). Radioactive Co isotopes are used in nuclear technology. Human activities which can cause Co contamination in the environment include coal burning, vehicle exhausts emissions, the use of phosphate fertilisers, mining, metalworks and nuclear facilities (ATSDR, 2004b). Environmental pollution problems from Co are generally less significant than those associated with some other heavy metals (Cole and Carson, 1981, cited in de Vos and Tarvainen, 2006).

Basic statistics and spatial distribution

Cobalt concentrations were determined using ICP-AES, with a method detection limit of 0.1 mg/kg. Co was detected at levels ranging from 0.39 mg/kg to 24.8 mg/kg, with a median value of 9.58 mg/kg. Cobalt levels in rural soils in the greater Dublin area as measured in retested NSDB samples range between 3.66 mg/kg and 12.4 mg/kg.

Concentrations of Co in topsoil appear to be influenced by both regional geology and human activities in the inner city. The spatial distribution of Co in the greater Dublin area (Figure 20) is similar to that of Ni, where higher concentrations occur in the northwest (Mulhuddart) and western inner city, possibly related to the presence of clayey minerals in the impure limestones. Median concentrations in topsoil overlying the sandstones, greywackes and shales of southwest Dublin are slightly higher than other bedrock types at around 11.2 mg/kg. The Cambrian metasediments of Howth Head and the Calendonian Granites in the southeast of the study area are relatively depleted in Co.

In terms of land zones, samples taken in areas of heavy industry had a slightly higher median level of Co than samples from other land zones at 10.4 mg/kg. This implies a possible influence of human activities on Co concentrations in the greater Dublin area.

Baseline

The spatial distribution of Co indicates areas of both anthropogenic and geogenic influences on soil Co. This observation is supported by the CP curve which shows a break between natural and anthropogenic near the centre of the line at approximately 11.5 mg/kg. Cobalt levels in rural NSDB soils in the Dublin area range between 3.7 mg/kg and 12.4 mg/kg.

Human health

Co is a component of Vitamin B12, which essential in the human diet. Most exposure to Co is to normal levels found in food. Exposure to excessive levels of Co usually only occurs through exposure to Co dust or radioactive Co associated with working in or living near industries which process Co or hazardous waste sites (ATSDR, 2004b). Such exposure can result in respiratory problems and skin allergies. The general public is unlikely to be exposed to Co in these ways. Cobalt is classed as a possible human carcinogen.

There is currently no UK CLEA SGV available for assessing risks to human health from soil Co concentrations.

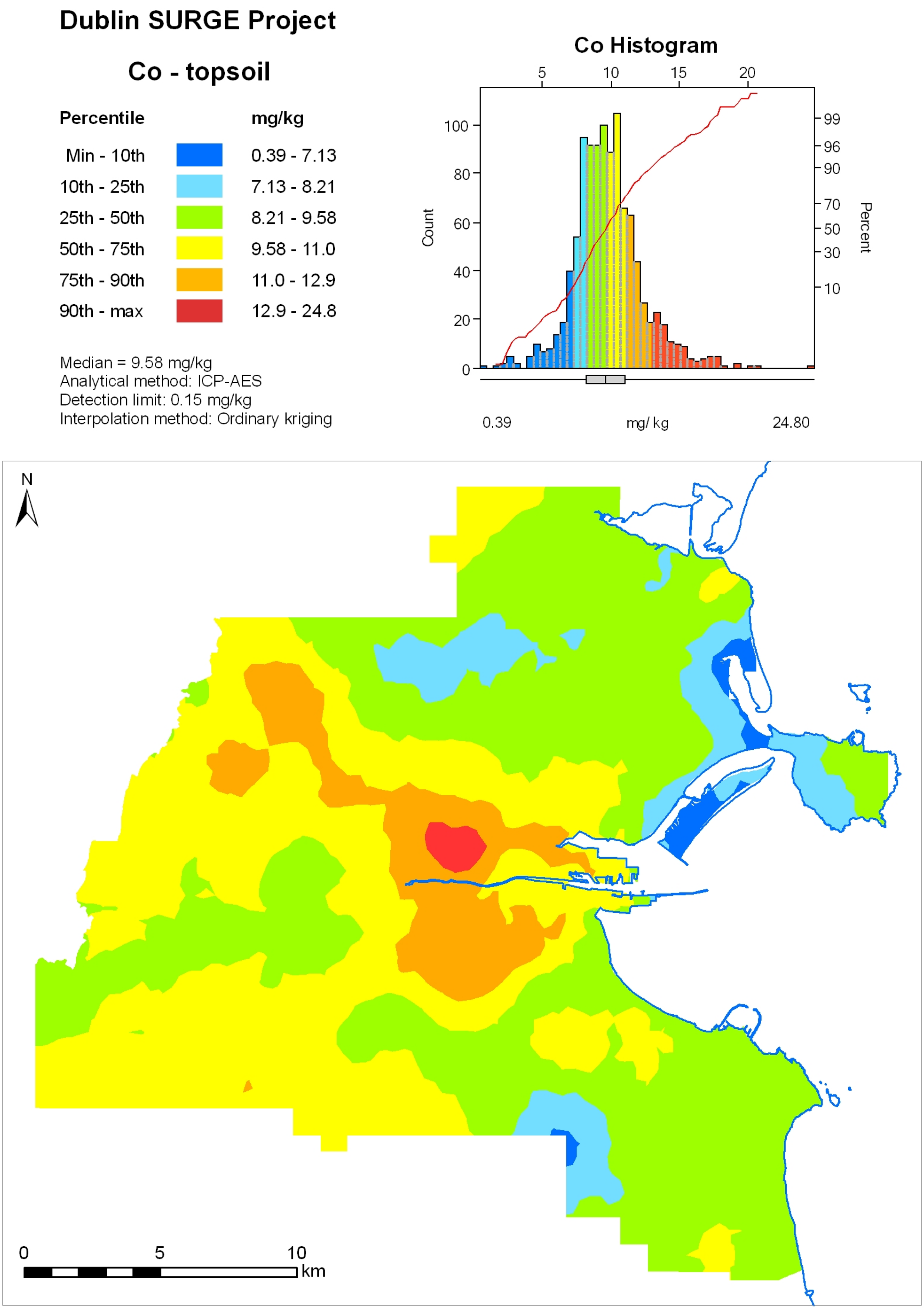


Figure 20 Topsoil Co concentrations in the greater Dublin area

6.1.5 Chromium -Cr

Cr is a hard, shiny grey metal which is produced from the ore chromite. Cr occurs in two oxidation states, as Cr^{3+} (Cr (III)) and Cr^{6+} (Cr (VI) or hexavalent chromium) (McGrath & Smith, 1990). Cr (VI) is toxic to humans and occurs mainly through industrial contamination. This study measured the total amount of Cr present in topsoils. The relative proportions of Cr (III) Cr (VI) were not determined.

Pure Cr is used in alloys including stainless steel. Cr (III) and Cr (VI) are used for chrome plating, pigments, wood preservatives, and in the leather tanning industry (ATSDR, 2008b). Human activities which release the most Cr into the environment include steel and iron production, coal burning, metal processing, tannery facilities and pigment production (McGrath & Smith, 1990; ATSDR, 2008b). Phosphate fertilisers are rich in Cr, with a range of 30-3,000 mg/kg Cr reported (McGrath & Smith, 1990).

Basic statistics and spatial distribution

Chromium concentrations were determined using ICP-AES, with a method detection limit of 0.3 mg/kg. Cr was detected at levels ranging from 4.24 mg/kg to 262 mg/kg, with a median value of 44.3 mg/kg.

The spatial distribution of Cr in the greater Dublin area (Figure 21) is influenced by regional geology, with possible influences from human activities. Higher levels of Cr in the north of the study area are probably associated with high shale content of the limestones in that area. The Cr content of limestone is normally low, but concentrations of Cr in shale worldwide can range from around 50 mg/kg to 1,500 mg/kg (Wedepohl, 1983).

Apart from hotspots in the inner city, Cr concentrations do not appear to be strongly related to human activity. Minor areas of elevated Cr occur in the Islandbridge-Crumlin area, Dublin Port and in a heavy industry zone in Coolock. Chromium levels in the Islandbridge-Crumlin area are likely to be geogenic in origin, as a similar pattern is observed in Ni concentrations. When the spatial distribution of Cr and Ni are similar, geogenic origin for the two metals is indicated. Chromium was formerly associated with tannery activities and there are records of eight 19th century tannery sites in the Merchant’s Quay/Crumlin area. However, this area has Cr concentrations under the median level, some 2km to the east of Islandbridge and does not account for the elevated Cr levels observed in the Islandbridge-Crumlin area.

Elevated Cr observed at Dublin Port and in the zone of heavy industry in Coolock are likely to be associated with industrial activities. Some individual soil samples in these areas have elevated Cr levels which correspond with high levels of Zn, Cd, Pb, and/or As, which can indicate the presence of toxic Cr(VI) (Rose *et al.,* 1979).

Median Cr concentrations are slightly elevated compared at allotments as compared to other sample location types, at 56.8 mg/kg. The use of phosphate fertilisers, which can be enriched with Cr, in allotments might account for the enrichments seen here.

Baseline

The spatial distribution of Cr indicates areas of both anthropogenic and geogenic influences on soil Co. This observation is supported by the CP curve which shows a break between natural and anthropogenic concentrations at approximately 60 mg/kg. Chromium levels in rural NSDB soils in the Dublin area range between 21.5 mg/kg and 59.1 mg/kg.

Human health

Cr (III) is an essential nutrient in the human diet required for normal energy metabolism (ATSDR, 2008b). However, Cr (VI) is toxic to humans and is associated with skin irritation and damage to the respiratory, gastrointestinal and male reproductive systems (ATSDR, 2008b). Cr (VI) is a known human carcinogen and is associated with cancer of the respiratory system, particularly the lungs, when inhaled (ATSDR, 2008b). In soil, Cr (III) is relatively stable, however Cr (VI) is more readily bioavailable (McGrath & Smith, 1990) and is more easily taken up by the human body. Cr (VI) is usually only present in soils due to industrial contamination (Fay *et al.,* 2007). It is recommended that for site specific investigations where elevated Cr levels are observed and/or the presence of Cr (VI) is suspected, speciated Cr testing is undertaken to identify the type of Cr present.

The main routes of exposure of the general population to Cr are through small quantities of Cr in food, water and air. People who work in or live near industries which use Cr and people who smoke cigarettes may be exposed to higher than normal levels of Cr (ATSDR, 2008b).

There is currently no UK CLEA SGV available for assessing risks to human health from soil Cr concentrations. It is likely that most Cr observed in Dublin topsoil is of geogenic origin. Elevated Cr concentrations in Dublin port area and in the Coolock area are likely to be related to industrial activities; however pathways for human exposure to soil contamination in these areas of heavy industry are limited.

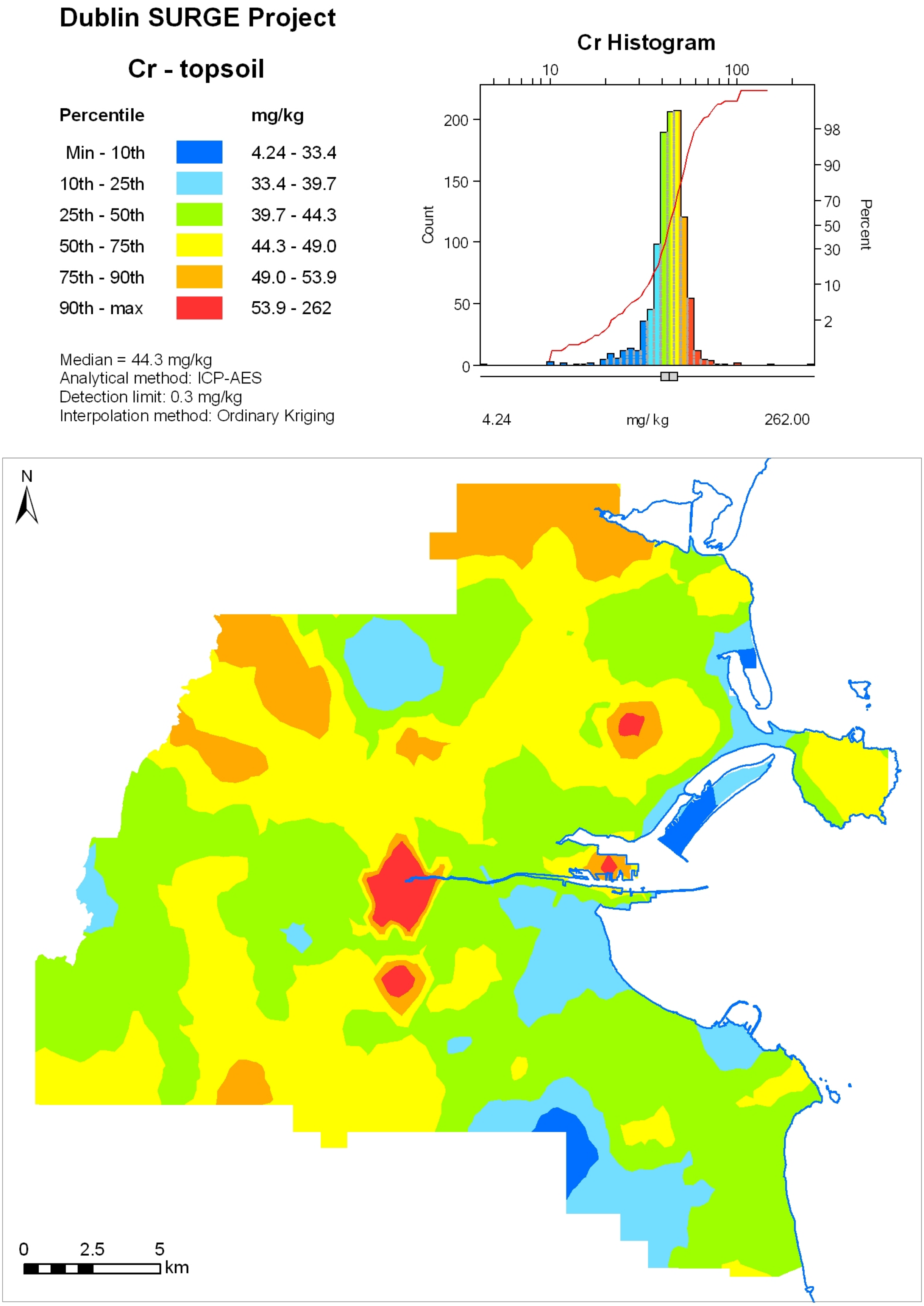


Figure 21 Topsoil Cr concentrations in the greater Dublin area

6.1.6 Copper - Cu

Copper is a reddish, malleable metal that occurs in many Cu mineral ores, most commonly chalcopyrite (Baker, 1990). Ireland has a long history of copper mining and there are three known Cu mineral localities in the greater Dublin area, at Robswalls, Porterstown and Corballis. Copper in the Meath-Dublin area occurs mainly in chalcopyrite veins associated with quartz and calcite minerals (McConnell *et al.,* 2001).

The main uses of Cu metal are in the production of pipes, wire, brass and bronze (Baker, 1990). Copper compounds are used in wood preservatives and nutritional supplements (ATSDR, 1993). Copper can be released into the environment through human activities such as fossil fuel burning, metallurgical and chemical industries and burning of waste containing Cu (Baker, 1990). The mean abundance of Cu in coal is 17 mg/kg, with significantly higher Cu concentrations contained in coal ashes (Wedepohl, 1983).

Basic statistics and spatial distribution

Cu concentrations were determined using ICP-AES, with a method detection limit of 1.5 mg/kg. Cu was detected at levels ranging from below the limit of detection to 6,480 mg/kg, with a median value of 35.0 mg/kg in the greater Dublin area. Results for one sample were below the limit of detection for Cu.

The spatial distribution of Cu in the greater Dublin area (Figure 24) is strongly influenced by human activity. Cu concentrations are highest in the city centre and concentrations decline concentrically with distance from the city centre. Boxplots of Cu by city zone (Figure 22) show that the median concentration of Cu is highest in the City Centre zone, at 76.6 mg/kg, followed by the Inner Suburban zone (40.7mg/kg) the Outer Suburban zone (30.5 mg/kg) and the Rural zone (28.85 mg/kg). This pattern reflects Dublin's long history of habitation and industry in the city centre area and the influence of those activities on the wider city environment. Anthropogenic activities which are likely to have contributed Cu to the inner city environment include coal burning, use of coal ash as fill material, industry and unregulated waste disposal.

Boxplots of Cu by land zone show that town centre and heavy industry zones have the highest median concentrations of Cu compared to other land zones, at 49.4 mg/kg and 54.6 mg/kg respectively (Figure 23). A locally elevated area of Cu in the Bluebell/Walkinstown area appears to be spatially related to a light industry zone in that area. The survey maximum for Cu of 6,840 mg/kg occurs in this area.

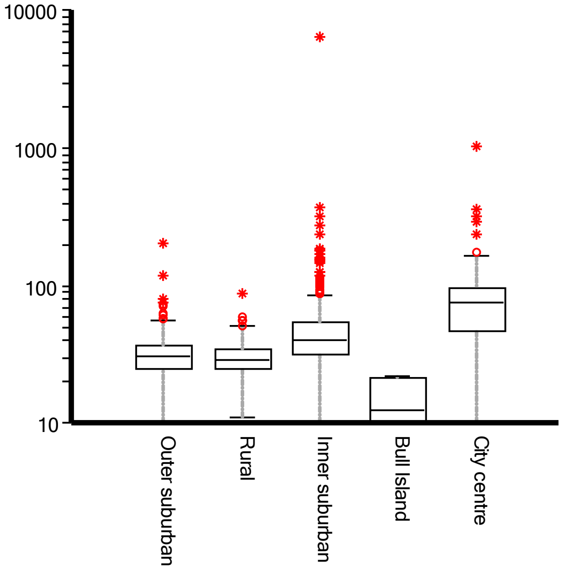


Figure 22 Copper boxplots by city zone

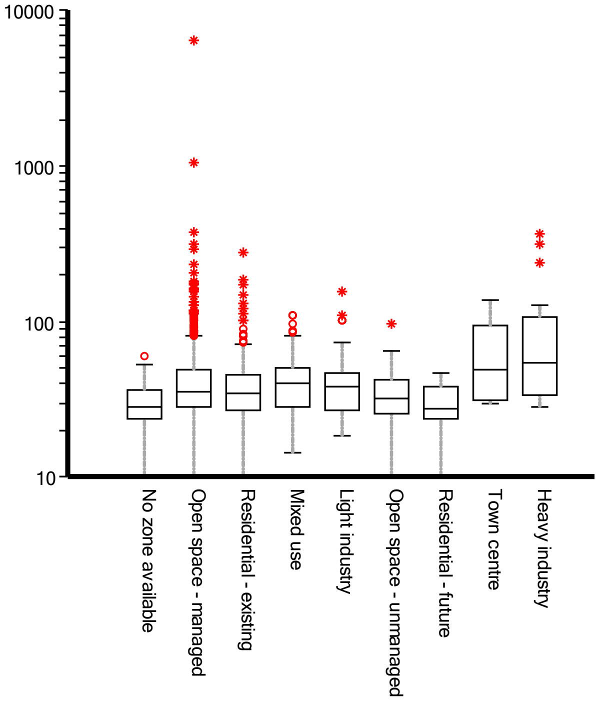


Figure 23 Copper boxplots by land use

Of the subsoil types in the study area, made ground had the highest median level of Cu at 46.35 mg/kg. It is likely that made ground in the inner city area contains elevated Cu concentrations due to the historical use of waste materials and fly ash as fill.

GSI records indicate Cu mineral occurrences at three locations in the greater Dublin area. Copper concentrations over the median level occurs around the Cu mineral location at Porterstown in west Dublin, which is likely to be related to natural Cu mineralisation in bedrock in that area. There is a minor area of locally elevated Cu concentrations near Malahide, which may be associated with historic Cu workings at Robswalls. It is also possible that Cu concentrations observed at Malahide are due to historic urban activity. An area of Cu enrichment is evident along the coast of Booterstown to Dún Laoghaire, which is possibly due to historic port activities or natural mineralisation in that area. The spatial distribution of Cu closely resembles that of Pb, with a strong Pearson correlation coefficient of 0.73.

Baseline

The spatial distribution and boxplots of Cu concentrations indicate a strong influence of inner city activities on soil Cu. The CP plot shows that the break between the natural and anthropogenic Cu concentrations occurs at approximately 50 mg/kg. Copper levels in rural NSDB soils in the Dublin area range between 13.2 mg/kg and 51.6 mg/kg.

Human health

Small amounts of Cu are essential for plants, animals and humans (ATSDR, 2004a). The general population is exposed to Cu as a normal part of the diet in food and water. Deficiencies or excesses of Cu in the human body can cause adverse health effects.

Harmful effects from exposure to excess Cu generally occur in relation to high Cu concentrations associated with working in or living near metallurgical industries such as smelters (ATSDR, 2004a). Adverse health effects such as gastrointestinal and respiratory distress have been reported in relation to the ingestion of Cu compounds and the inhalation of Cu dust (ATSDR, 2004a). Cu is not considered carcinogenic to humans.

There is currently no UK CLEA SGV available for assessing risks to human health from soil Cu concentrations. The highest values of Cu observed in the study area are in industrial areas, where there are limited pathways for exposure of the general public to soil.

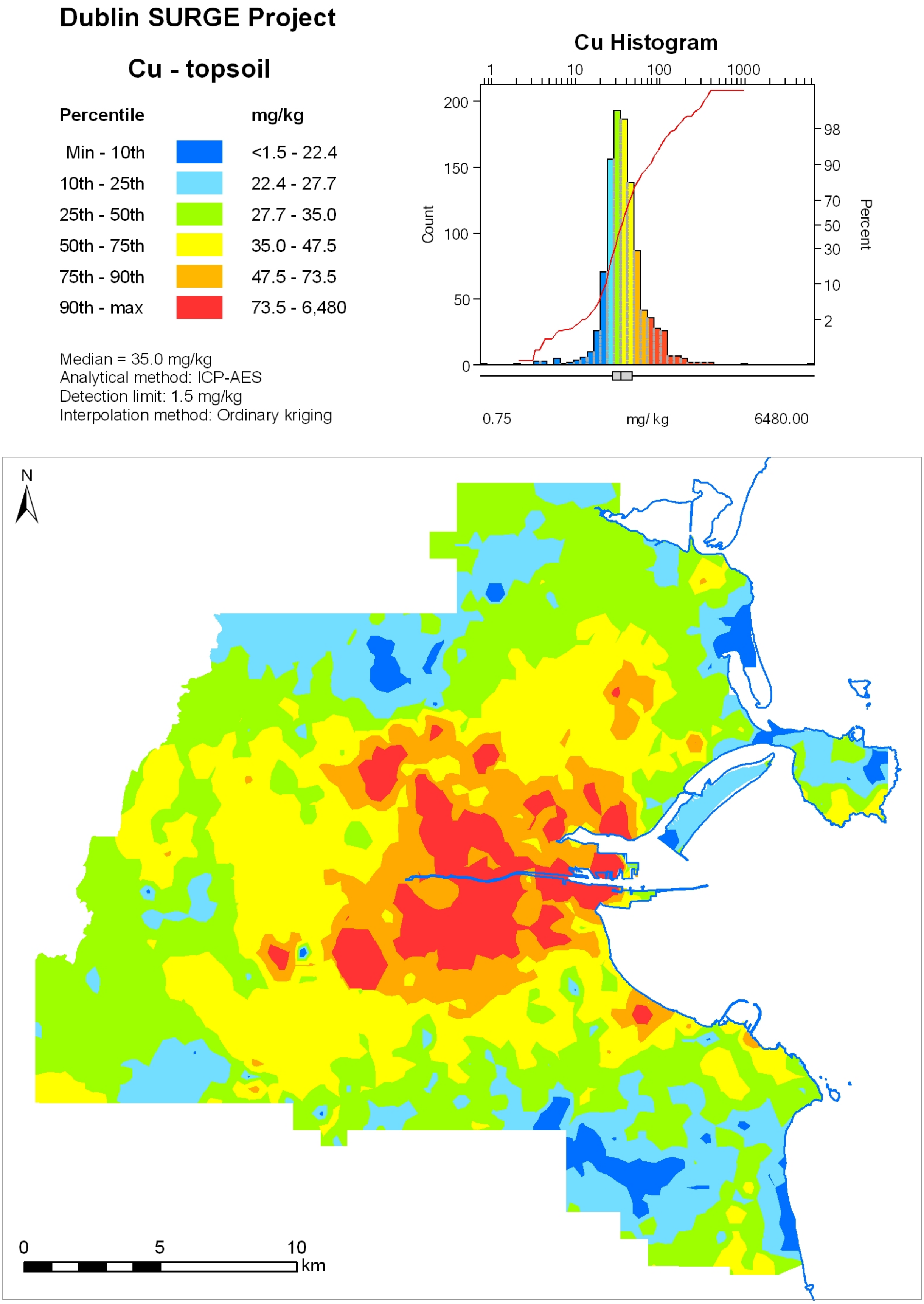


Figure 24 Topsoil Cu concentrations in the greater Dublin area

6.1.7 Mercury - Hg

In its elemental form, Hg is a dense, silvery metal which is a volatile liquid at room temperature (UK EA, 2009c). The most important source of mercury is the naturally occurring mineral, cinnabar (HgS) (UK EA, 2009c). Levels of Hg in the earth's crust are generally low, however, coal and argillaceous (clayey) rocks and sediments can be enriched with Hg (Kabata-Pendias and Mukherjee (2007), cited in UK EA (2009c)).

Mercury is naturally released into the environment through the erosion of Hg-containing rocks and soils and from volcanic activity (ATSDR, 1999). It is estimated that human activities such as mining, fossil fuel (especially coal) burning, mining, smelting, waste incineration, cremation and cement production emit between one third and two thirds of all annual Hg releases into the environment (ATSDR, 1999).

Combustion processes involving fossil fuels, metals and minerals can emit trace elements such as Hg to the atmosphere which in turn can be deposited in soils. The most significant worldwide emitter of Hg is coal-burning power generation. The production and use of Hg is being phased out in Europe and the US, whereas global Hg emissions continue to rise due to the increase of coal-fired power generation and industry in developing countries (EUROPA, 2008).The chlor-alkali industry, which uses Hg in the production of chlorine gas and caustic soda from salt, is the biggest consumer of Hg in Europe (EUROPA, 2008). Cremation of human remains releases Hg from dental fillings. It is estimated that up to 16% all mercury emitted in the UK is sourced from the vaporisation of Hg from dental fillings during cremation (UK DEFRA, 2004). There are three crematoria in the greater Dublin area, at Glasnevin, Mount Jerome and Newlands Cross. Unregulated landfilling or burning of materials containing Hg can also contribute Hg to soils. Hg adheres strongly to soils and aquatic sediments and is generally immobile in water (ATSDR, 1999).

Elemental Hg readily combines with other inorganic elements to form inorganic Hg compounds (salts) and with carbon to form organic Hg compounds such as methylmercury (UK EA, 2009c). Elemental Hg is used in thermometers, barometers, light switches, paints, alkali batteries and dental fillings (ATSDR, 1999). Historically, elemental Hg was used in the recovery of gold and silver from ores and for curing pelts to make hats. Inorganic Hg compounds have been used as fungicides, medicinal antibacterial agents and as dyes (ATSDR, 1999). Mercury can be changed from one form to another by microbial activity in soils. Most methylmercury present in soils is produced by microbial activity. Total Hg, which includes elemental, inorganic and organic forms of Hg were measured in this study.

Basic statistics and spatial distribution

Total Hg concentrations were determined using cold vapour atomic absorption spectrometry, with a method detection limit of 0.0075 mg/kg. Mercury was detected at levels ranging from 0.014 mg/kg to 23.9 mg/kg, with a median value of 0.206 mg/kg in the greater Dublin area. Mercury levels in rural soils in the greater Dublin area as measured in retested NSDB samples range between 0.087 mg/kg and 0.593 mg/kg.

The spatial distribution of Hg in the greater Dublin area (Figure 26) is strongly influenced by human activity. Mercury concentrations are highest in the city centre and concentrations decline concentrically with distance from the city centre. Boxplots of Hg by city zone (Figure 25) show that the median concentrations of Hg are highest in the City Centre zone, at 0.56 mg/kg, followed by the Inner Suburban zone (0.28 mg/kg) the Outer Suburban zone (0.16 mg/kg) and the Rural zone (0.12 mg/kg). Anthropogenic activities which are likely to have contributed Hg to the inner city environment include coal burning, cremation, industry and unregulated waste disposal.

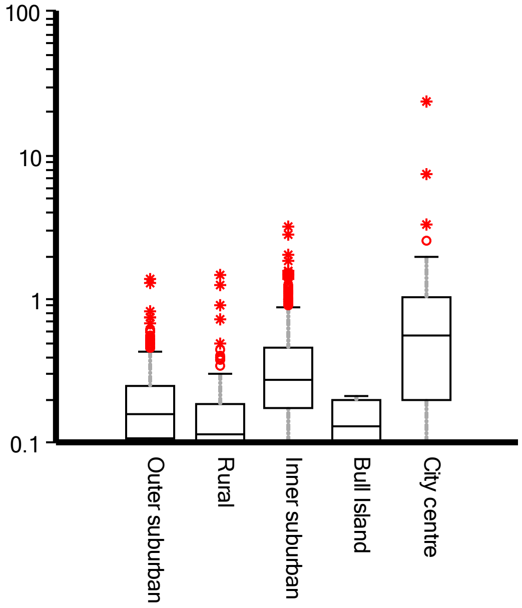


Figure 25 Mercury boxplots by city zone

Crematoria are potentially a modern source of Hg emissions in Dublin. There is no obvious enhancement of Hg soil concentrations in the immediate vicinity of the three crematoria. However, Glasnevin and Mount Jerome are located in an inner city area with concentrations of Hg over the 90th percentile level, and Newlands Cross is located in an area with Hg concentrations over the median level. It is possible that soil in these areas received emissions from the crematoria, as well as diffuse emissions from historical inner city sources.

In terms of land use, town centre and mixed use zones have the highest median concentrations of Hg compared to other land zones, at 0.29 mg/kg and 0.27 mg/kg respectively. A localised zone of Hg above the median level occurs in the vicinity of the Pb mineral location at Porterstown in west Co. Dublin. Hg is associated with some of the Pb-Zn deposits present throughout the midlands and with the sulphide deposits in Wicklow (Fay *et al.,* 2007).

Baseline

The spatial distribution and boxplots of Hg concentrations indicate a strong influence of inner city activities on soil Hg. The CP plot shows that the break between the natural and anthropogenic Hg concentrations occurs at approximately 0.2 mg/kg. Mercury levels in rural NSDB soils in the Dublin area range between 0.087 mg/kg and 0.59 mg/kg. However, the Soil Geochemical Atlas of Ireland notes that Hg concentrations in the Dublin and Wicklow regions are elevated (>0.15 mg/kg) due to urban and mining activities (Fay *et al.,* 2007). Hence the range seen in the retested NSDB samples may represent above-background Hg concentrations. This observation, along with the strong concentric zonation of Hg concentrations from the inner city to the survey boundaries, indicates long range diffuse pollution sources which have imparted low-level Hg contamination to the Dublin region.

Human health

The general population is exposed to small quantities of natural Hg in the environment but additional exposure mainly occurs via dental fillings, minor Hg spills in the home (due to e.g.

broken thermometers), and the consumption of fish from Hg-contaminated waters (ATSDR, 1999). Methylmercury is highly bioaccumulative and can build up in freshwater and marine mammals and fish to levels that are many times greater than the surrounding water (ATSDR, 1999).

Elemental liquid Hg is readily adsorbed as vapours by the lungs through inhalation, but is poorly adsorbed via dermal contact and oral ingestion (ATSDR, 1999). The oral route is a more significant pathway for the other forms of mercury, with approximately 40% of inorganic forms and 90% of methymercury adsorbed by the gastrointestinal system when ingested (ATSDR, 1999). On entering the body Hg is converted to different forms and can stay in the body from weeks to months (ATSDR, 1999). Exposure to Hg is associated with adverse effects to the kidneys and to the cardiovascular, gastrointestinal, musculoskeletal and central nervous systems (ATSDR, 1999). Mercury chloride and methylmercury are classed as possible human carcinogens.

The UK CLEA guidance gives three SGVs for Hg (Table 7), relating to the different exposure pathways and toxicities for elemental, inorganic and organic Hg forms (UK EA, 2009c). The SGV for elemental Hg only considers the inhalation route, while the oral, dermal and inhalation routes are taken into account for inorganic and organic forms. As part of this project total soil Hg content was determined, which includes all forms of Hg. UK CLEA advises that in the absence of separate determinations of elemental, inorganic and methylmercury concentrations, total Hg content can be compared to the inorganic Hg SGV. It is beyond the scope of this study to make assessments of the risk to human health from Hg concentrations on individual sites without detailed site-specific information. However, the results are compared to the UK SGVs to give an overview of soil quality in Dublin in relation to Hg.

Concentrations of Hg measured in this study do not exceed the inorganic Hg SGVs (80 mg/kg for allotments, 170 mg/kg for residential land use and 3,600 for commercial/industrial land use). The maximum concentration of Hg measured was 23.9 mg/kg. On this basis of this generalised assessment, no exceedances of SGVs are identified from Hg concentrations observed in this study. At individual sites the occurrence of high concentrations of elemental Hg or methylmercury may exceed the respective SGVs for those forms. Site-specific investigations are recommended for sites where the existence of elemental mercury or methylmercury in soils is suspected or confirmed due to human activities.

	UK CLEA SGVs for Hg, mg/kg		
	Elemental	**Inorganic**	**Methylmercury**
Residential	1	170	11
Allotment	26	80	8
Commercial/industrial	26	3,600	410

Table 7 UK CLEA human health criteria for Hg

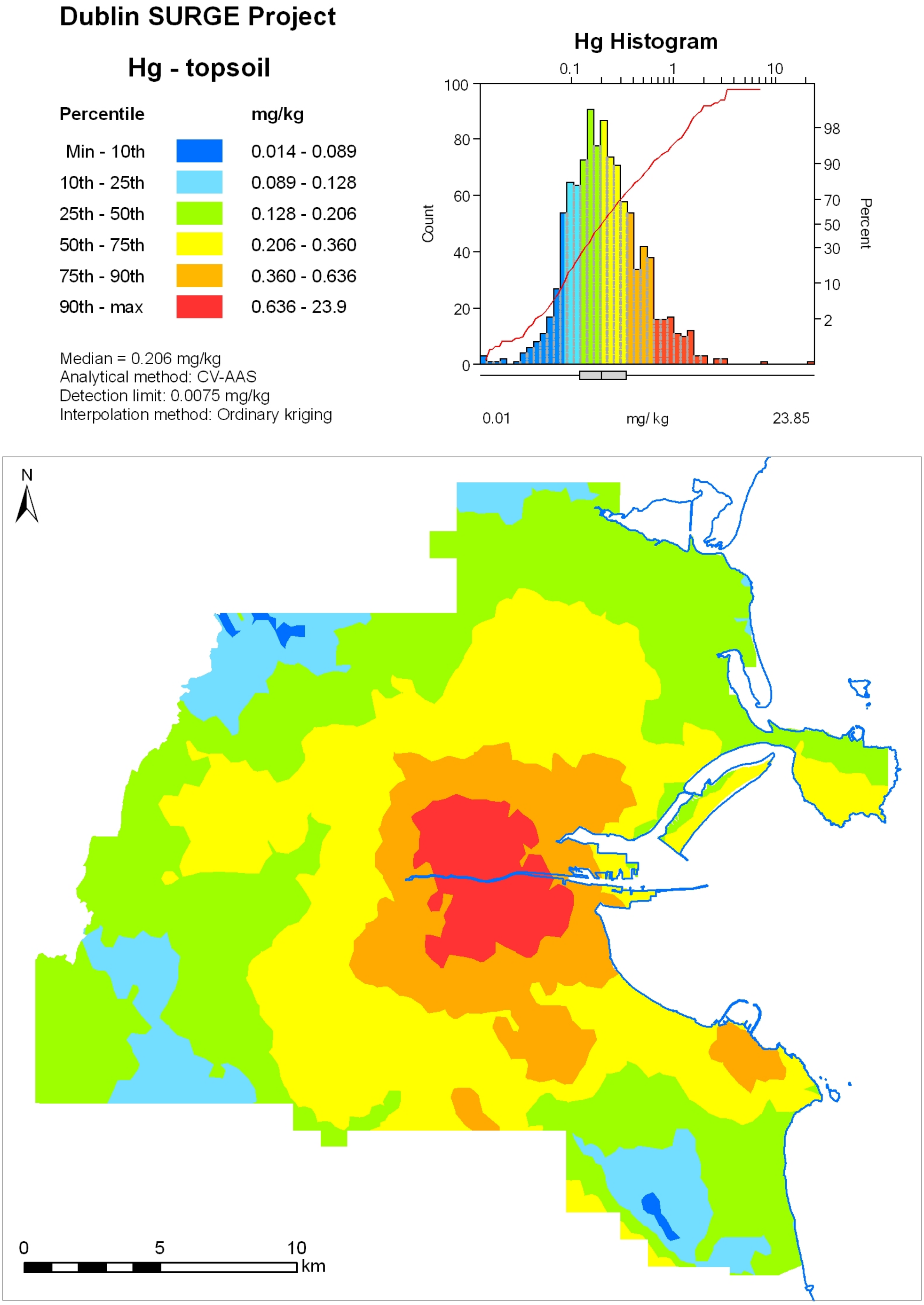


Figure 26 Topsoil Hg concentrations in the greater Dublin area

6.1.8 Nickel – Ni

Pure Ni is a hard, silver-white metal (ATSDR, 2005a). Pure Ni occurs rarely in nature and is normally found in mineralised areas in association with iron and sulphur compounds (UK EA, 2009d).

Most Ni is used in the production of stainless steel. Nickel is commonly used as an alloy with other metals such as iron, copper, chromium and zinc in the production of coins, jewellery and industrial metal products (ATSDR, 2005a). Nickel combines with many other inorganic elements to form nickel compounds, which are used in nickel plating, pigments and batteries and as chemical catalysts (ATSDR, 2005a).

Human activities which can cause Ni contamination include burning of fossil fuels, Ni mining and smelting, refuse incineration and spreading of sewage sludges (McGrath & Smith, 1990). Coals and fly ash can be enriched with Ni (McGrath & Smith, 1990). Oil contains more Ni than coals; diesel oil combustion produces particulate emissions high in Ni (McGrath & Smith, 1990).

Basic statistics and spatial distribution

Nickel concentrations were determined using ICP-AES, with a method detection limit of 1.5 mg/kg. Nickel was detected at levels ranging from 5.5 mg/kg to 145 mg/kg, with a median value of 41.0 mg/kg. Nickel levels in rural soils in the greater Dublin area as measured in retested NSDB samples range between 11.7 mg/kg and 50.3 mg/kg.

The spatial distribution of Ni in the greater Dublin area (Figure 28) is strongly influenced by regional geology, with possible influences from human activities in the inner city. The Soil Geochemical Atlas of Ireland (Fay et al., 2007) notes natural enrichments (over 37.5 mg/kg) of Ni in an area encompassing counties Westmeath, Meath, Kildare and Dublin, which are attributed to naturally high Ni levels in impure limestones. Ni levels are normally very low in limestones (Wedepol, 1983), but the high shale content of the Lucan Formation in this area may account for the Ni enrichments observed. The Ni-enriched band of impure limestone stretching from the midlands to Dublin is evident in the study area in the northwest (Mulhuddart), and western inner city (Crumlin, Glasnevin, Finglas). Median concentrations in the Calp limestone are slightly higher than other bedrock types at around 43.15 mg/kg (Figure 27). The Cambrian metasediments of Howth Head and the Calendonian Granites in the southeast of the study area are notably depleted in Ni.

The inner city concentrations do not appear to be spatially related to historic residential and industrial areas of the city or the port, as seen with other anthropogenic metals. There are no strong trends relating Ni concentrations to any particular land use zone or city zone. Overall the distribution of Ni is quite similar to that of Cd, with a strong Pearson correlation coefficient of 0.71.

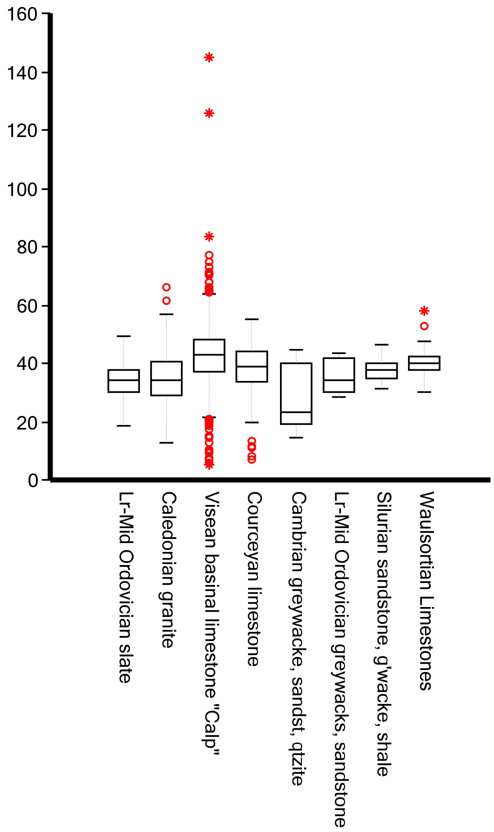


Figure 27 Nickel boxplots by bedrock type

Baseline

The spatial distribution of Ni indicates that soil Ni is mainly determined by regional geology, with influences from anthropogenic activity in inner city industrial areas. This CP curve shows a break between natural and anthropogenic concentrations at approximately 55 mg/kg. Nickel levels in rural NSDB soils in the Dublin area range between 11.7 mg/kg and 50.3 mg/kg.

Human health

The most commonly reported adverse health effect of Ni is allergic dermatitis (ATSDR, 2005a). Nickel can cause allergic skin reactions in sensitised people following either dermal or oral exposure (UK EA, 2009d). The use of Ni in products which come into regular contact with skin such as jewellery, watch straps, zips and buttons has been restricted in the EU for this reason (UK EA, 2009d).

The main routes of exposure of the general population to Ni are through food consumption and smoking (ATSDR, 2008a). Although it contributes only a small amount to total Ni exposure, Ni in house dust (tracked in from outdoor soil) is a significant pathway for exposure pathway in residential settings (UK EA, 2009d). People who live near, or work in Ni-emitting industries may be exposed to higher levels of Ni in dust and soil. Dust containing high levels of Ni compounds is carcinogenic to the lungs and nasal tissues in humans (UK EA, 2009d). Such dusts are not normally encountered in the environment and are associated with occupational exposure of workers at metalworks etc. Based on animal studies, it is thought that Ni may also have adverse effects on the reproductive and developmental systems in humans (UK EA, 2009d).

The UK CLEA guidance gives SGVs for Ni in residential, allotment and commercial land uses (Table 8). It is beyond the scope of this study to make assessments of the risk to human health from Ni concentrations on individual sites without detailed site-specific information. However, the results are compared to the UK SGVs to give an overview of soil quality in Dublin in relation to Ni.

Only one soil sample (145 mg/kg) located in the inner city area exceeds the SGV for Ni in residential land use. This sampling location is in an area of light industry so human exposure pathways to soil in this area are likely to be more limited than those in a residential setting. Most of the Ni observed in Dublin soils is expected to be geogenic in origin, due to natural enrichments of Ni in the Dublin Basin limestones. Much of the Ni found in air, soil, sediment, and rock is so strongly attached to dust and soil particles or embedded in minerals that it is not readily taken up by plants and animals and, therefore, cannot easily affect human health (ATSDR, 2005a).

No soil samples measured as part of the Dublin SURGE Project exceed the Ni SGVs for allotment or commercial land uses.

Land use	SGV for Ni (mg/kg)	No. of exceedances
Residential	130	1
Allotment	230	None
Commercial	1800	None

Table 8 UK CLEA SGVs for Ni

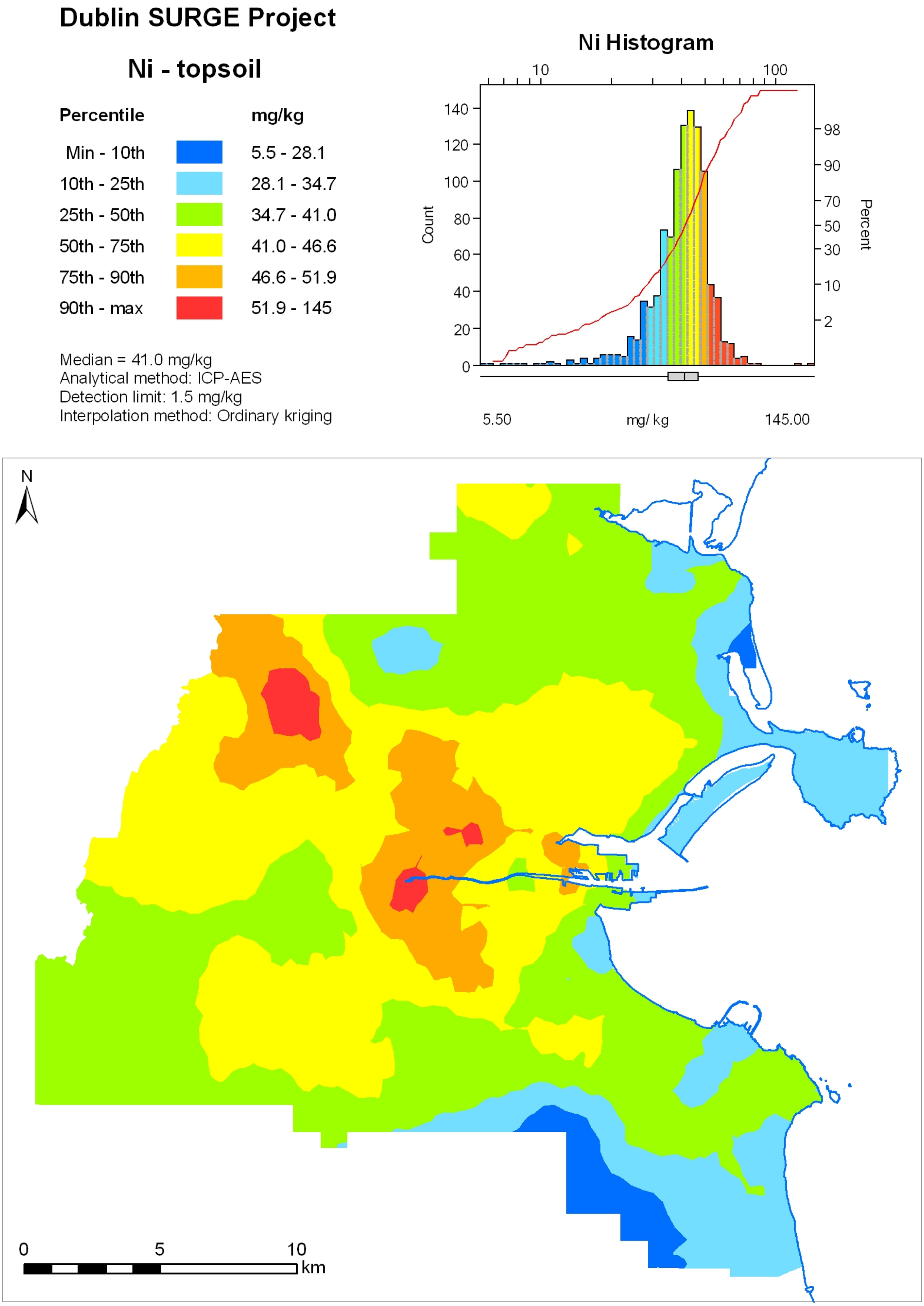


Figure 28 Topsoil Ni concentrations in the greater Dublin area

6.1.9 Lead - Pb

Lead is a dense, blue-grey coloured metal that occurs naturally primarily as the mineral galena (PbS) (ATSDR, 2007a). It is a soft metal with a low boiling point, meaning that historically it was readily mined, smelted and worked for a variety of purposes. Lead has been used in batteries, ammunition, water supply pipes and roofing materials; as an additive to paint, petrol and pesticides; and in the manufacture of glass, pottery and ceramics. Lead can be deposited in soils due to landfilling or burning of such materials. Weathering of buildings painted with Pb paint can contribute flakes of Pb paint into nearby soils.

Combustion processes such as the leaded petrol combustion, smelting and Pb metalworks can emit Pb particles to the atmosphere which in turn can be deposited in soils. Many studies (cited in Davies, 1990) have established a strong correlation between Pb in roadside soils and traffic due to the emission of lead particles in traffic fumes and in dust from engine and tyre wear.

UK coals are known to contain significant amounts of Pb and the combustion of such coal releases Pb and other coal-derived trace elements into the environment as particulate emissions and fly ash (Fuge, 2005).

Although the use of leaded petrol and lead paint and burning of bituminous coal have been phased out in Ireland, Pb from these sources is persistent and sources remain in surfaces painted with lead paint, building materials and waste disposal.

Basic statistics and spatial distribution

Lead concentrations were determined using ICP-AES, with a method detection limit of 3 mg/kg. Pb was detected at levels ranging from below the limit of detection to 3,120 mg/kg, with a median value of 73.7 mg/kg in the greater Dublin area. Results for 0.1% of the samples were below the limit of detection for Pb.

The spatial distribution of Pb in the greater Dublin area (Figure 30) is strongly influenced by human activity. Lead concentrations are highest in the city centre and decline concentrically with distance from the city centre. The median concentration of Pb is highest in the City Centre zone, at 216 mg/kg, followed by the Inner Suburban zone (98.3 mg/kg) the Outer Suburban zone (56.7 mg/kg) and the Rural zone (49 mg/kg). This pattern reflects Dublin’s long history of habitation and industry in the city centre area and the influence of those activities on the wider city environment. The strong concentric zonation implies a longterm diffuse atmospheric deposition source for Pb.

Other urban soil Pb studies from around the world have demonstrated the same increase of Pb concentrations with proximity to the city centre (cited in Davies, 1990). Anthropogenic activities which are likely to have contributed Pb to the inner city environment include traffic, unregulated waste disposal, weathering of old Pb paint on structures and coal burning. There may also be urban sources of Pb in Malahide and Dún Laoghaire, both of which have long histories of habitation.

Boxplots of Pb by land zone (Figure 29) show that town centre and heavy industry zones have the highest median concentrations of Pb compared to other land zones, at 178 mg/kg and 174 mg/kg respectively. Of the subsoil types in the study area, made ground had the highest median level of Pb at 129.5 mg/kg (112 samples). It is likely that made ground in the inner city area contains elevated Pb concentrations due to the historical use of waste materials and fly ash as fill.

GSI records indicate Pb mineral occurrences at nine locations in the greater Dublin area, associated with Pb mineralisation in both the Dublin Basin limestones and along the margin of the Leinster Granites. Concentrations of Pb above the median level occur around minor Pb workings or mineral occurrences in the limestone at Porterstown, Palmerstown and Clontarf. Carboniferous limestones at Navan, Co. Meath some 50km northwest of Dublin host a major Zn-Pb deposit which is exploited at Tara Mines.

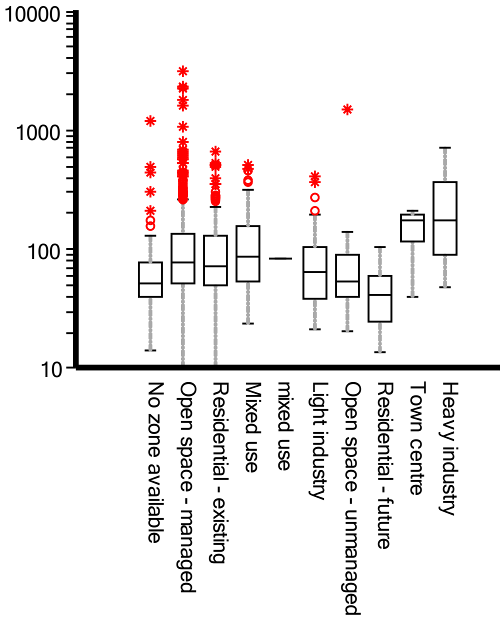


Figure 29 Lead boxplots by Land Zone

Concentrations of Pb over the median level also occur in the south county Dublin coastal area and are associated Pb mineralisation in a northeast trending band along the eastern margin of the Leinster Granite (McConnell, 1994). Three Pb mineral localities occur in this zone at Mount Malpas (Killiney), Rathmichael and Ballycorus. At Ballycorus Pb and Ag were mined and smelted, and exposed waste piles remain at the site with high concentrations of Pb (median values exceeding 1.5%) (Stanley *et al.*, 2009). A zone of elevated Pb in the coastal Booterstown to Monkstown area may be due to a previously unidentified area of mineralisation.

Baseline

The spatial distribution and boxplots of Pb concentrations indicate a strong influence of inner city activities on soil Pb. However Dublin is also located in an area of known Pb mineralisation, so it is difficult to determine a clear break between natural and anthropogenic concentrations on the CP plot. It is suggested that the break between anthropogenic and natural concentrations is in the region of 80-110 mg/kg. Lead levels in rural NSDB soils in the Dublin area range between 30.8 mg/kg and 120 mg/kg.

Further understanding of natural, local and long range anthropogenic Pb pollution sources could be gained by carrying out Pb isotope analysis on soil samples. Such analysis allows links to be made between different types of soil Pb and different emission sources.

Human health

Lead is persistent in the environment and it tends to accumulate in surface soils due to its low solubility and resistance to microbial degradation (Davies, 1990).

For the general population, the primary exposure route to Pb is oral (ATSDR, 2007a), i.e. via food, the ingestion of soil and indoor dust, consumption of homegrown vegetables and ingestion of soil attached to vegetables. Children are more vulnerable to adverse health impacts from Pb than adults; exposure effects include neurological impairment, growth retardation and anaemia (ATSDR, 2007a). Following exposure in adults, 99% of ingested Pb is excreted by the body; in children, only 32% is excreted as waste (ATSDR, 2007a). Pb remaining in the body moves through the blood to soft tissues and organs in the body. After a number of weeks, it accumulates mainly in the bones and teeth, where it can stay for decades (ATSDR, 2007a). Lead and Pb compounds are considered probable human carcinogens, based on animal studies (ATSDR, 2007a).

There is currently no UK CLEA SGV available for assessing risks to human health from soil Pb concentrations. In 2008 the UK CLEA soil guideline value for Pb was withdrawn pending an updated approach. Former values were 450 mg/kg for allotment and residential land use, and 750 mg/kg for commercial and industrial land use (UK EA, 2002).

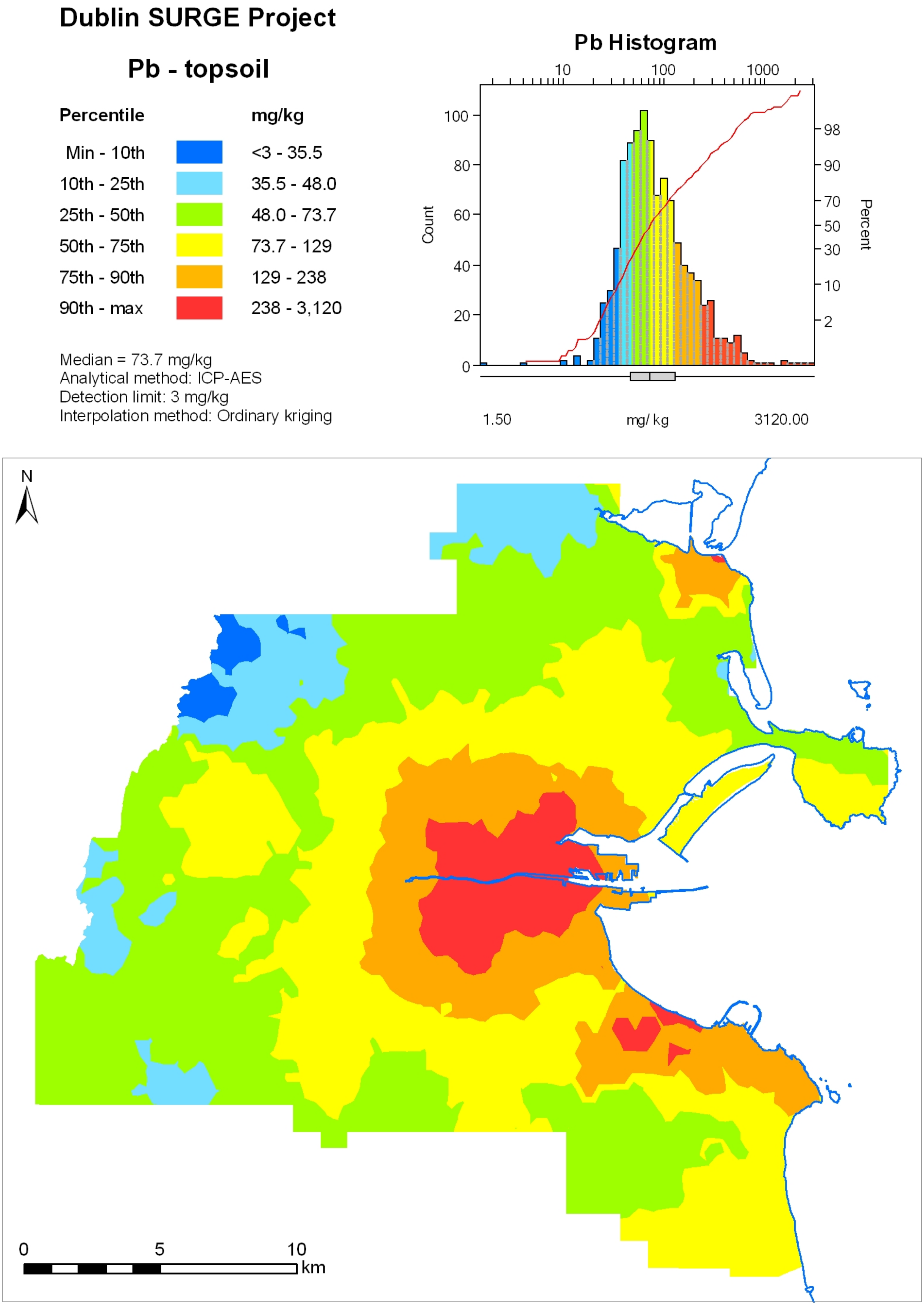


Figure 30 Topsoil Pb concentrations in the greater Dublin area

6.1.10 Vanadium - V

Pure V is a bright white, soft and ductile metal (ATSDR, 2009). Vanadium is relatively abundant and is found in about 65 different minerals including camotite, vanadinite, roscoelite and patronite (UK EA, 2010b). The average V content of carbonate rocks is low, with higher values occurring in greywackes, shales and clays (de Vos and Tarvainen, 2006). The highest V concentrations occur in mafic rocks such as basalt.

Vanadium and its compounds are used in metal alloys, ceramics, electronics and dietary supplements (ATSDR, 2009 and UK EA, 2010b). Anthropogenic sources of V contamination include coal and oil combustion, steel alloy production and traffic emissions (de Vos and Tarvainen, 2006). Coal and oil combustion and the disposal of their ash represent the biggest contribution of anthropogenic V to the environment (Jones *et. al.,* 1990). Vanadium is the major trace element in coal and in petroleum products, particularly in the heavier fractions such as crude oil (Jones *et. al.,* 1990). Wedepohl (1983) reports that the V content of coal is variable, with a worldwide average content in hard coal of 19 mg/kg and 126 mg/kg in fly ash.

Basic statistics and spatial distribution

Vanadium concentrations were determined using ICP-AES, with a method detection limit of 1.5 mg/kg. Vanadium was detected at levels ranging from 10.8 mg/kg to 114 mg/kg with a median value of 72.1 mg/kg in the greater Dublin area. Levels of V in rural soils in the greater Dublin area as measured in retested NSDB samples range between 35.0 mg/kg and 88.6 mg/kg.

Concentrations of V in topsoil appear to be mainly determined by regional geology. Vanadium has very strong correlations (Pearson correlation coefficient of >0.82) with the predominantly geogenic metals Al, Fe, Ni, Sc, and Y. Slightly higher median values of V occur in topsoil overlying the limestones in northern and western Dublin compared to topsoil overlying other bedrock types (74.4 mg/kg). Vanadium is relatively depleted in soil over the Leinster granites.

Despite the association between coal and oil burning and V contamination of soils, there are not strong indications that V concentrations in Dublin are influenced by human activity, i.e. V concentrations are not higher in inner city or industrial areas. This may be due to the use of coals and fuel oils that have naturally low concentrations of V. The survey maximum occurs in an area of reclaimed land in Fairview, which could be related to contaminated fill materials, possibly fly ash.

Baseline

The spatial distribution of V indicates that soil V is mainly determined by regional geology, with minor influences from anthropogenic activity in isolated areas Figure 31. This CP curve shows a break between natural and anthropogenic concentrations at approximately 87 mg/kg. Vanadium levels in rural NSDB soils in the Dublin area range between 35.0 mg/kg and 88.6 mg/kg.

Human health

Vanadium is an essential nutrient for many animals (de Vos and Tarvainen, 2006). Most human exposure to V is through natural levels found in foods. When exposed to levels much higher than those naturally found in the environment, people can experience respiratory irritation and adverse effects to the gastrointestinal and haematological systems (ATSDR, 2009). Such levels are normally only encountered in occupational settings or near hazardous waste sites. Vanadium is considered possibly carcinogenic to humans based on animal tests (ATSDR, 2009). There is currently no UK CLEA SGV available for assessing risks to human health from soil V concentrations. Concentrations of V above the median level occur mainly in north and western Dublin and are considered to be naturally occurring in the impure limestones.

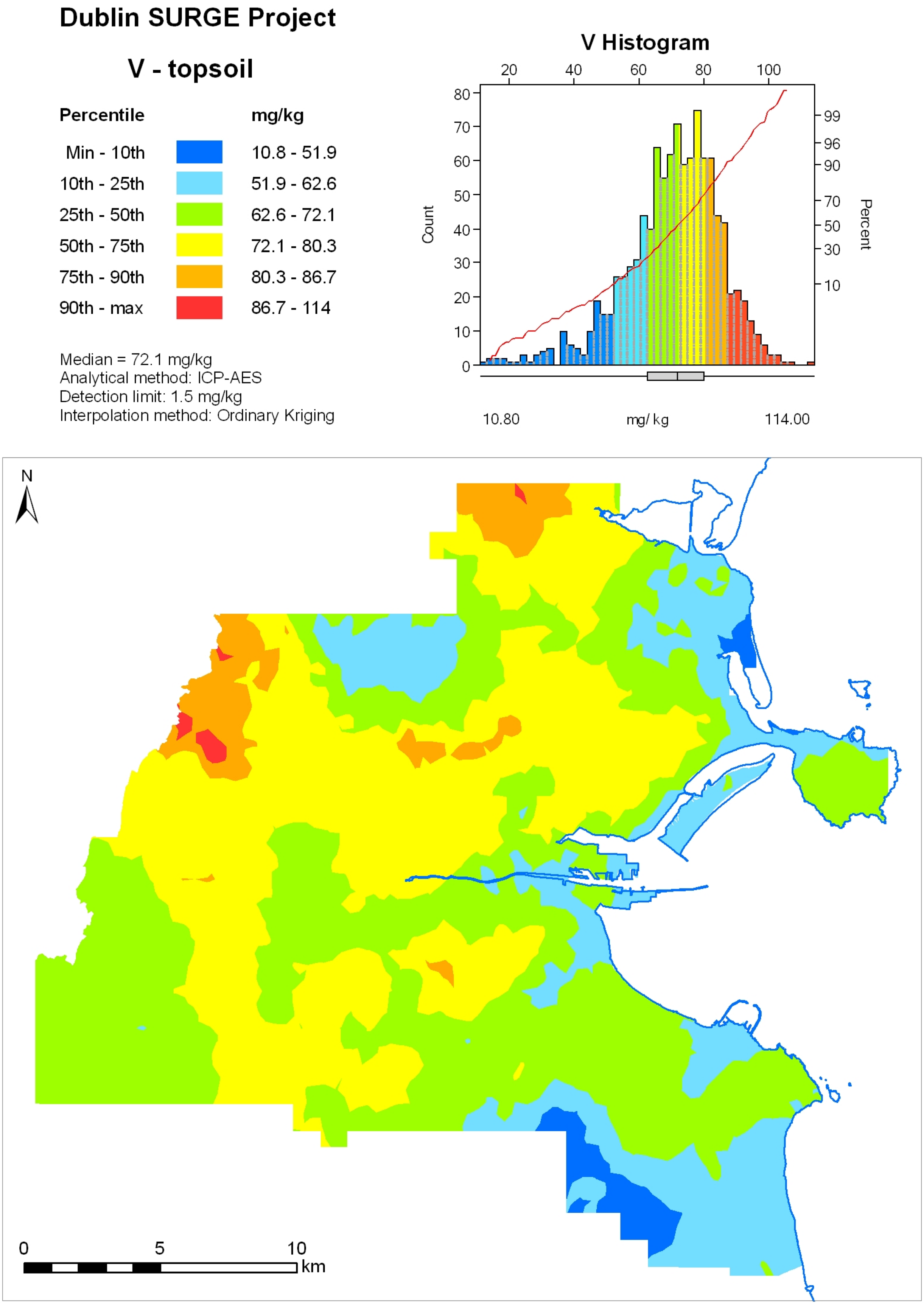


Figure 31 Topsoil V concentrations in the greater Dublin area

6.1.11 Zinc - Zn

Pure Zn is a hard, brittle bluish-white metal (ATSDR, 2005b). Zinc is abundant in the environment and most Zn is found in the Zn sulphide ore sphalerite (ZnS) (ATSDR, 2005b). Europe's largest zinc mine is located in Ireland, at Tara Mines, near Navan, Co. Meath, some 50km northwest of Dublin. Lower Carboniferous limestones of the Navan Group yield 8.4% Zn and 2.1% Pb in sphalerite and galena minerals (McConnell *et al.,* 2001).

Zinc is most commonly used as a galvanising coating for metals, in alloys and in batteries (ATSDR, 2005b; Fay *et al.,* 2007). Human activities which can cause Zn contamination include burning of fossil fuels, Pb mining and smelting, refuse incineration and spreading of sewage sludges (ATSDR, 2005b). Coal, oil and fly ash can contain Zn; coal often contains Zn in the concentration range 50 - 150 mg/kg (Wedepohl, 1983). Zinc is a significant component of tyre tread and Zn can accumulate in roadside soils due to tyre wear (ATSDR, 2005b).

Basic statistics and spatial distribution

Zinc concentrations were determined using ICP-AES, with a method detection limit of 3 mg/kg. Zn was detected at levels ranging from 18 mg/kg to 8,390 mg/kg, with a median value of 172 mg/kg. Levels of Zn in rural soils in the greater Dublin area as measured in retested NSDB samples range between 69.5 mg/kg and 205 mg/kg.

The spatial distribution of Zn in the greater Dublin area (Figure 34) is influenced by both regional geology and human activities, particularly in the port area.

The Soil Geochemical Atlas of Ireland (Fay *et al.,* 2007) notes natural enrichments (over 120 mg/kg) of Zn in topsoil in an area encompassing counties Westmeath, Meath, Kildare and Dublin, which are attributed to naturally high Zn levels in impure limestones. This Zn-enriched band of impure limestone is evident in the study area, where elevated concentrations of Zn in topsoil are extensive, with a median concentration of Zn in soils overlying limestone of 185 mg/kg. GSI records indicate a mineral location in the Calp at Wyanstown, some 10km north of the survey boundary. Enrichments of Zn are also evident in metasediments of southwest Co. Dublin, along the western margin of the Leinster granites. This is area is located in a region of bedrock mineralisation relating to the Leinster granite intrusion. The median concentration of Zn in Mid-Lower Ordovician metasediments in this area is 202 mg/kg.

Zinc concentrations are elevated in the Dublin docklands and port areas and in an area of heavy industry in Coolock. Since soils in the docklands and port are composed of made ground, it is likely that the Zn levels are due to anthropogenic contamination. The median concentration of Zn in made ground was the highest of the subsoil types sampled, at 234.5 mg/kg. The three highest Zn concentrations measured in the survey were located in the port (North Wall) and the median for samples taken in areas of heavy industry including the port was significantly higher than the other land zones sampled, at 821 mg/kg Zn (Figure 32).

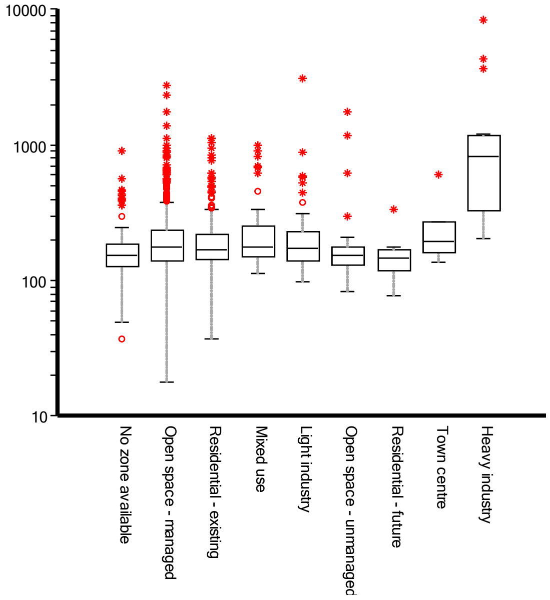


Figure 32 Zinc boxplots by land zone

Possible sources of anthropogenic Zn in made ground in the docklands area include coal fly ash, industrial waste and dust from Zn ore storage and transport. Zinc and Pb ores from Tara Mines are exported to smelters in mainland Europe via Alexandra Basin in Dublin port (Boliden, 2010; Dublin Port Company, 2010). Enrichments of Zn in the inner city may be due to tyre and engine wear from traffic, contaminated fill materials and fossil fuel combustion. Enrichments of Zn and other heavy metals in a heavy industry zone in Coolock are possibly the results of industrial contamination.

Where recycled tyre products are used in urban open spaces such as parks, playing fields and playgrounds, it is possible that they could contribute to Zn in soils. Studies have showed that Zn can readily leach from used tyres (Horner, 1996), tyre debris (Gualtieri *et al.*, 2005) and tyre crumb (Bocca *et al.*, 2009) under laboratory conditions. Further work is required to assess the impacts of tyre products in the urban environment.

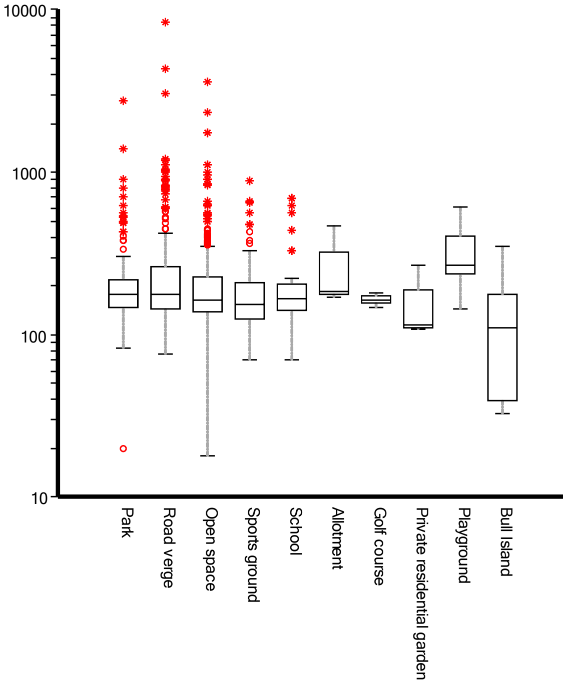


Figure 33 Zinc boxplots by location type

Baseline

The spatial distribution and boxplots of Zn concentrations indicate a strong influence of inner city activities on soil Zn. The CP plot indicates that the break between anthropogenic and natural concentrations is approximately 200 mg/kg. Zinc levels in rural NSDB soils in the Dublin area range between 69 mg/kg and 205 mg/kg. Areas with concentrations over 200 mg/kg are likely to be associated with anthropogenic contamination or Zn mineralisation.

Human health

Small amounts of Zn are essential for plants, animals and humans (ATSDR, 2005b). Deficiencies or excesses of Zn in the human body can cause adverse health effects. Harmful effects from exposure to excess Zn in the diet generally occur at Zn levels 10-15 times higher than normal Zn levels (ATSDR, 2005b). Longterm excess ingestion of Zn is associated with anaemia and adverse effects on cholesterol levels. Inhaling large amounts of Zn dust or fumes can cause acute respiratory problems. Exposure to very high levels of Zn are most likely to occur in occupational settings or by breathing, drinking contaminated drinking water, touching soil, or eating contaminated soil near sites contaminated with Zn.

There is currently no UK CLEA SGV available for assessing risks to human health from soil Zn concentrations. It is unlikely that a child would ingest enough zinc from eating soil to cause harmful effects (ATSDR, 2005b). The highest values of Zn observed in the study area are in areas of heavy industry, where there are limited pathways for exposure of the general public to soil.

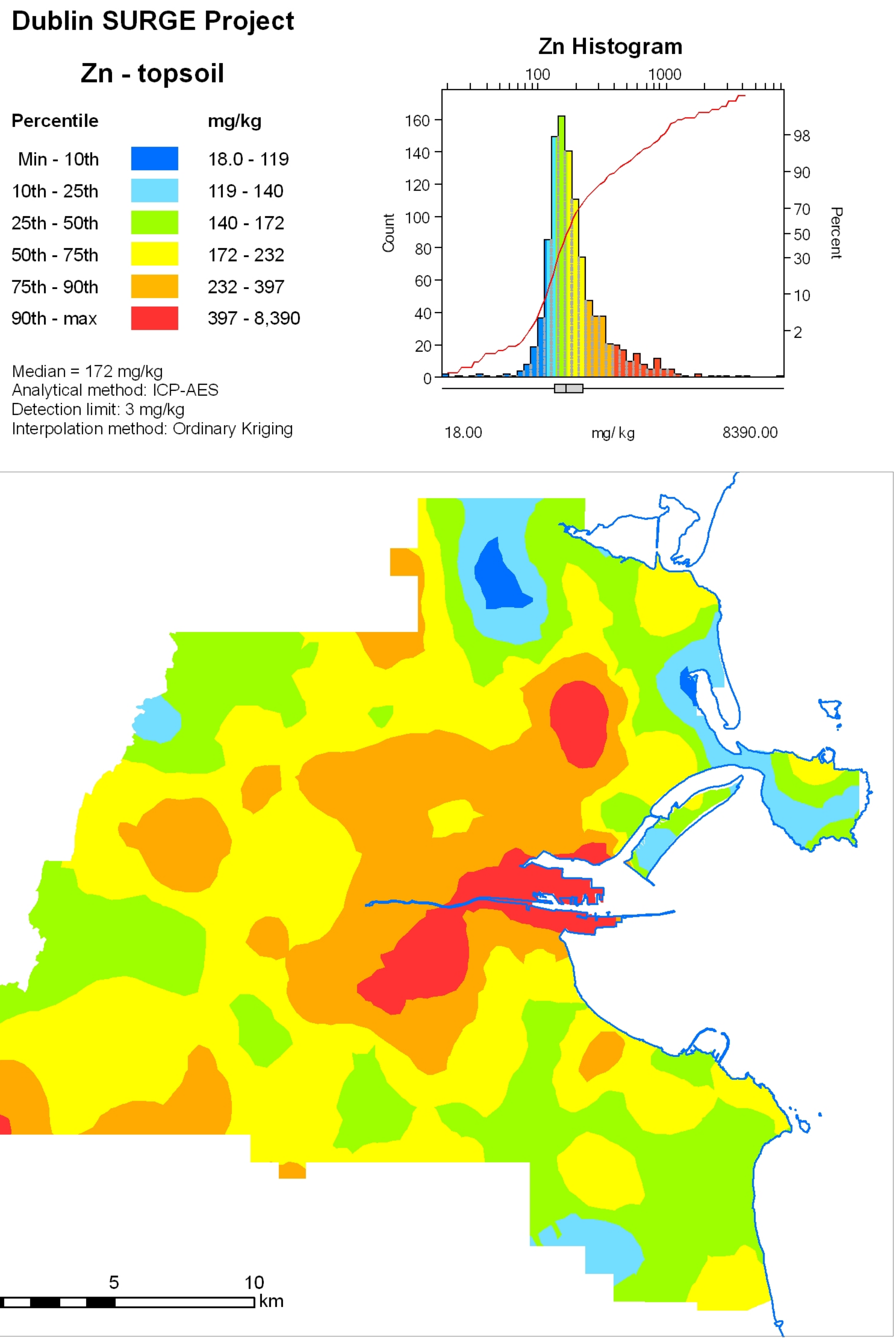


Figure 34 Topsoil Zn concentrations in the greater Dublin area

6.1.12 Geogenic metals interpretation

Aluminium – Al

Aluminium is the most abundant metal in the earth’s crust. It is a lightweight metal used in beverage cans, pots and pans, foil and in roofing materials and planes. Aluminium compounds are used in cosmetics and medicines (ATSDR, 2008c).

Aluminium concentrations were determined using ICP-AES, with a method detection limit of 250 mg/kg. Due to the abundance of Al in soils, results are reported as a percentage of the dry weight of soil instead of mg/kg (1% is equivalent to 10,000 mg/kg). Al was detected at levels ranging from 0.136 % to 5.55% with a median value of 2.88% in the greater Dublin area (Figure 35).

Levels of Al in rural soils in the greater Dublin area as measured in retested NSDB samples range between 2.11% and 3.64%. The Soil Geochemical Atlas of Ireland notes natural enrichments (over 4%) of Al in the east of the country, associated with igneous rocks, schists and shales (Fay *et al.,* 2007).

Concentrations of Al over the median level are possibly associated with naturally occurring Al levels in impure limestones/shales in the west of the study area and in argillaceous rocks around the margin of the Leinster granite and at Howth Head. Aluminium and other inorganic elements are relatively depleted in inner city and coastal areas. This trend is discussed in Section 6.1.13.

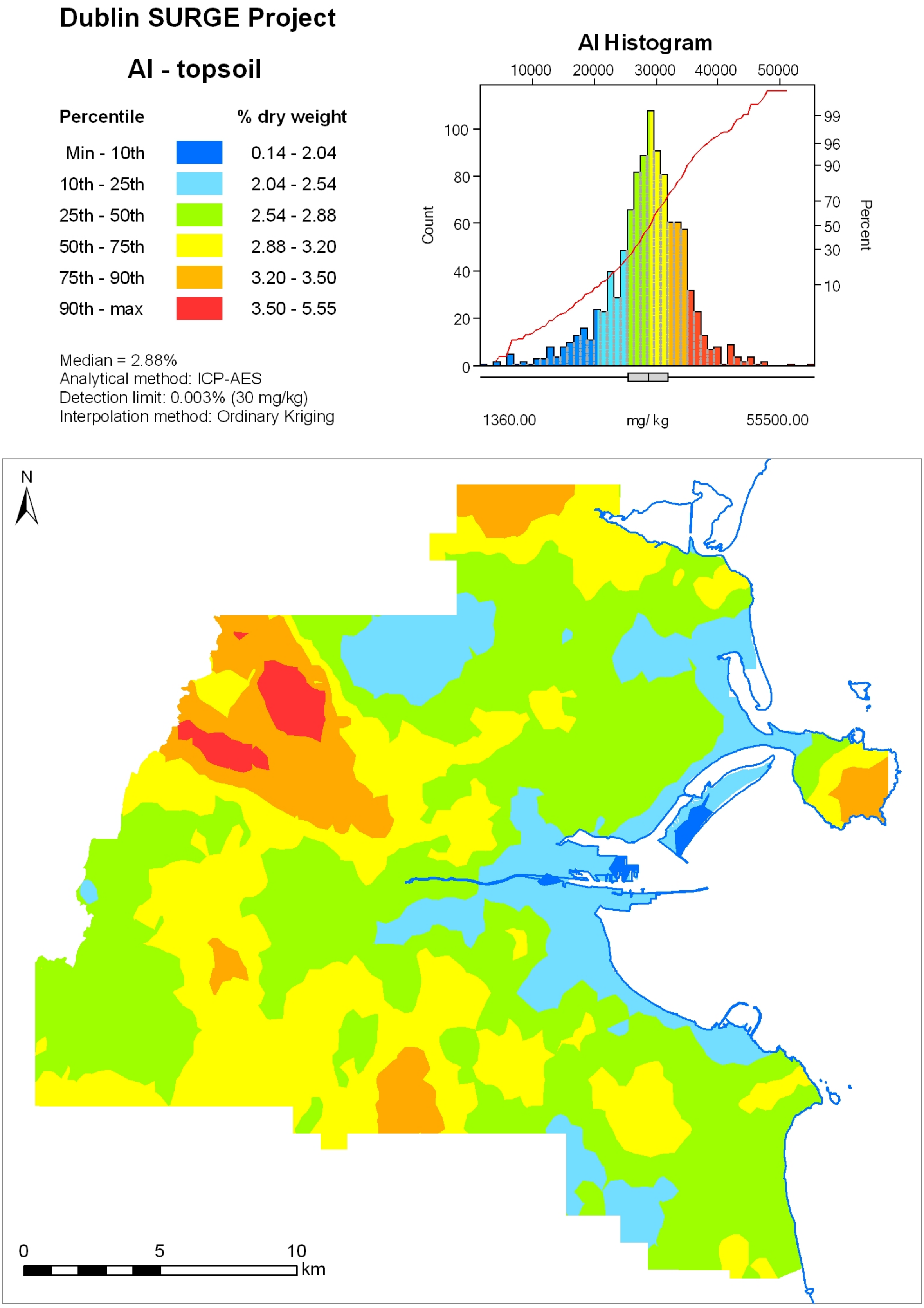


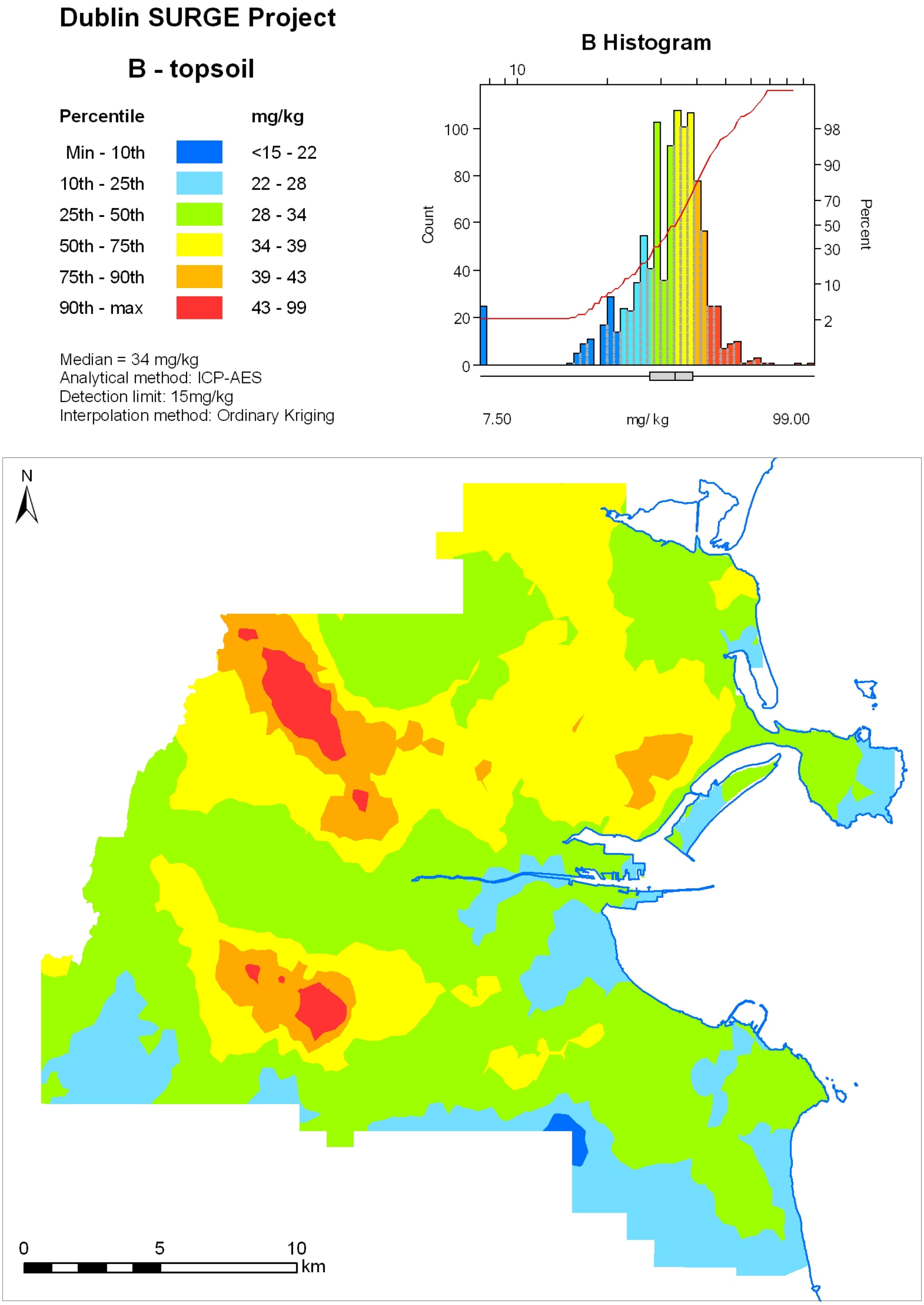
Figure 35 Topsoil Al concentrations in the greater Dublin area

Boron – B

Boron is a metalloid element, meaning that it has physical and chemical properties intermediate between metals and nonmetals. It is found primarily in the environment combined with oxygen in compounds called borates (ATSDR, 2010). Borates are used in glass, ceramics, detergents, fire retardants and pesticides (ATSDR, 2010).

Boron concentrations were determined using ICP-AES, with a method detection limit of 15 mg/kg. Boron was detected at levels ranging from below the method detection limit to 99 mg/kg, with a median value of 34 mg/kg in the greater Dublin area (Figure 36). Levels of B in rural soils in the greater Dublin area as measured in retested NSDB samples range between 15 mg/kg and 43 mg/kg.

Concentrations of B over the median level in the west and north of the study area are possibly associated with naturally occurring B enrichments in impure limestones/shales.



Dublin SURGE Project

B - topsoil

Percentile		mg/kg
Min - 10th	🟦	<15 - 22
10th - 25th	🟦	22 - 28
25th - 50th	🟩	28 - 34
50th - 75th	🟨	34 - 39
75th - 90th	🟧	39 - 43
90th - max	🟥	43 - 99

Median = 34 mg/kg
Analytical method: ICP-AES
Detection limit: 15mg/kg
Interpolation method: Ordinary Kriging

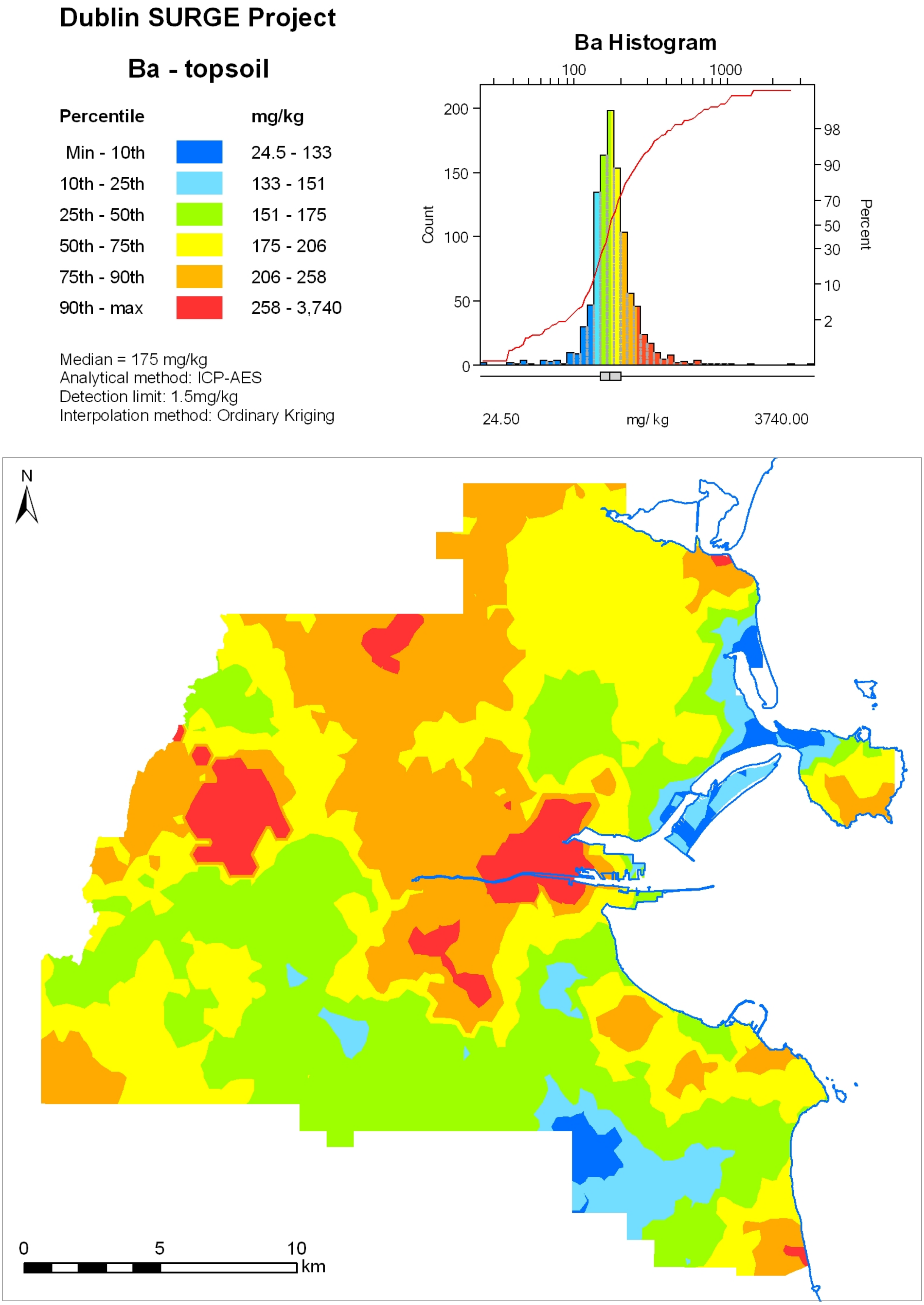
Figure 36 Topsoil B concentrations in the greater Dublin area

Barium – Ba

Barium is a silvery white metal which is only found in ores as Ba compounds. Barium compounds are used to make lubricating slurrys for oil and gas drilling, and are used in paint, bricks, ceramics, glass and rubber (ATSDR, 2007).

Barium concentrations were determined using ICP-AES, with a method detection limit of 1.5 mg/kg. Barium was detected at levels ranging from 24.5 mg/kg to 3,740 mg/kg, with a median value of 175 mg/kg in the greater Dublin area (Figure 37). Levels of Ba in rural soils in the greater Dublin area as measured in retested NSDB samples range between 94.2 mg/kg and 271 mg/kg. The Soil Geochemical Atlas of Ireland (Fay *et al.,* 2007) notes that Ba may be somewhat elevated in limestones, especially in areas of mineralisation. Barium commonly occurs in association with Pb and Zn in Carboniferous limestones of the Dublin Basin.

Concentrations of Ba over 200 mg/kg are widespread in topsoil in the northwest Dublin area. Barytes (Ba minerals) are known to occur naturally in limestone in this area; GSI records indicate a baryte mineral location at a quarry in Balseskin. Barium levels over the 90th percentile level occur in the Porterstown area in west Dublin, where there is a known Pb mineral location. The highest recorded level of Ba occurs in the city centre, where there may be an influence of human activities on Ba levels. Ba can be introduced into the environment through fossil fuel burning and industry (Fay *et al.,* 2007). Ba is relatively depleted in topsoil overlying the Leinster Granites and on Bull Island.



Median = 175 mg/kg
Analytical method: ICP-AES
Detection limit: 1.5mg/kg
Interpolation method: Ordinary Kriging

Figure 37 Topsoil Ba concentrations in the greater Dublin area

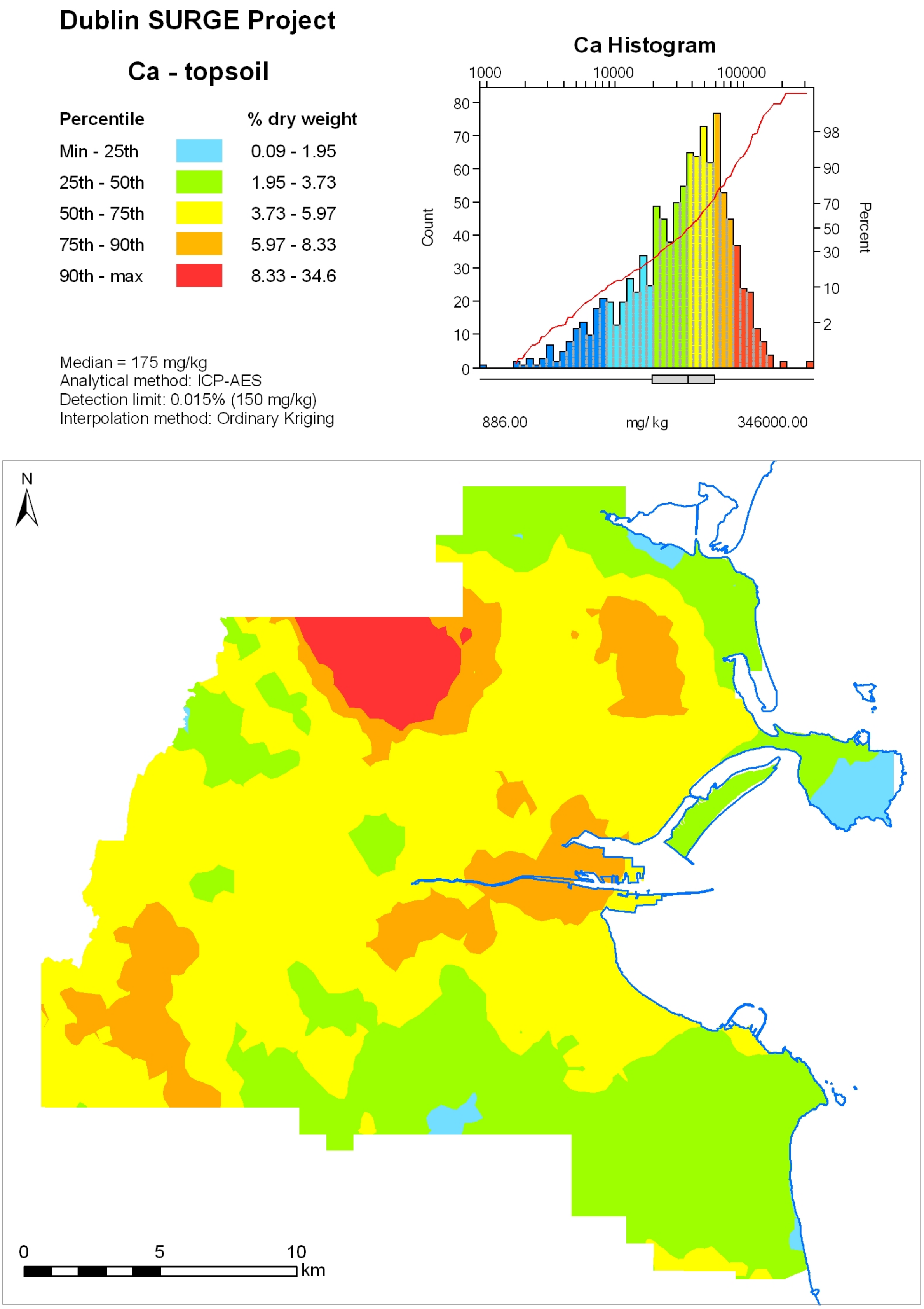
Calcium – Ca

Calcium is a soft grey alkaline metal. Calcium is the fifth most abundant element in the earth's crust and it forms a large number of minerals, some of which are major constituents of rocks (Wedepohl, 1983). Sedimentary rocks such as limestone are abundant in Ca minerals such as calcite. Ca is an essential element for humans and animals, where it mostly stored in teeth and bones (Fay *et al.,* 2007).

Calcium concentrations were determined using ICP-AES, with a method detection limit of 0.015% (150 mg/kg). Calcium is very abundant in soils, especially in limestone regions, therefore results are reported as a percentage of the dry weight of soil instead of mg/kg. Ca was detected at levels ranging from 0.08% to 34.6%, with a median value of 3.73% in the greater Dublin area (Figure 38). Levels of Ca in rural soils in the greater Dublin area as measured in retested NSDB samples range between 0.24% and 3.46%. The Soil Geochemical Atlas of Ireland (Fay *et al.,* 2007) notes that concentrations of Ca of up to 27% are associated with limestone areas.

Concentrations of Ca over the median level of 3.18% occur in limestone areas in the Dublin basin area, in the centre, north and west of the study area. This is consistent with the expectation that soil in limestone areas is enriched with Ca. Three quarries are located in Huntstown, which is located in an area of natural Ca enrichment which may be associated with calcite mineralisation in a bedrock fracture zone. Limestone is or has been quarried at numerous locations within the study area. The historic industries database records some 220 limestone quarries and 77 lime kilns in the study area. These activities, along with the modern use of construction and demolition rubble for filling ground, may account for the enriched Ca levels in the inner city.

Calcium correlates strongly with Sr, with a Pearson correlation coefficient of 0.94. Strontium can substitute for Ca in carbonate minerals in limestones (de Vos and Tarvainen, 2006). Calcium is relatively depleted in topsoil overlying the Leinster Granites and Cambrian metasediments of Howth Head.



Median = 175 mg/kg
Analytical method: ICP-AES
Detection limit: 0.015% (150 mg/kg)
Interpolation method: Ordinary Kriging

Figure 38 Topsoil Ca concentrations in the greater Dublin area

Cerium – Ce

Cerium is the most abundant of the rare earth elements (De Vos & Tarvainen, 2006). High Ce levels in rocks are associated with intrusive granites and argillaceous sedimentary rocks (De Vos & Tarvainen, 2006). Cerium is not known to have any biological role and is mainly used in metal alloys, glass, ceramics and in petroleum refining (De Vos & Tarvainen, 2006).

Cerium concentrations were determined using ICP-AES, with a method detection limit of 3 mg/kg. Cerium was detected at levels ranging from 4 mg/kg to 55.8 mg/kg with a median value of 31.9 mg/kg in the greater Dublin area (Figure 39). Levels of Ce in rural soils in the greater Dublin area as measured in retested NSDB samples range between 31.2 mg/kg and 42.7 mg/kg.

The spatial distribution of Ce closely resembles that of Al, i.e. it is relatively depleted in inner city and coastal areas. Cerium concentrations over the 90th percentile level occur in association with the Leinster Granites in south Co. Dublin. Other areas of Ce enrichment occur in west and north Dublin possibly with impure limestones in the Dublin Basin area.

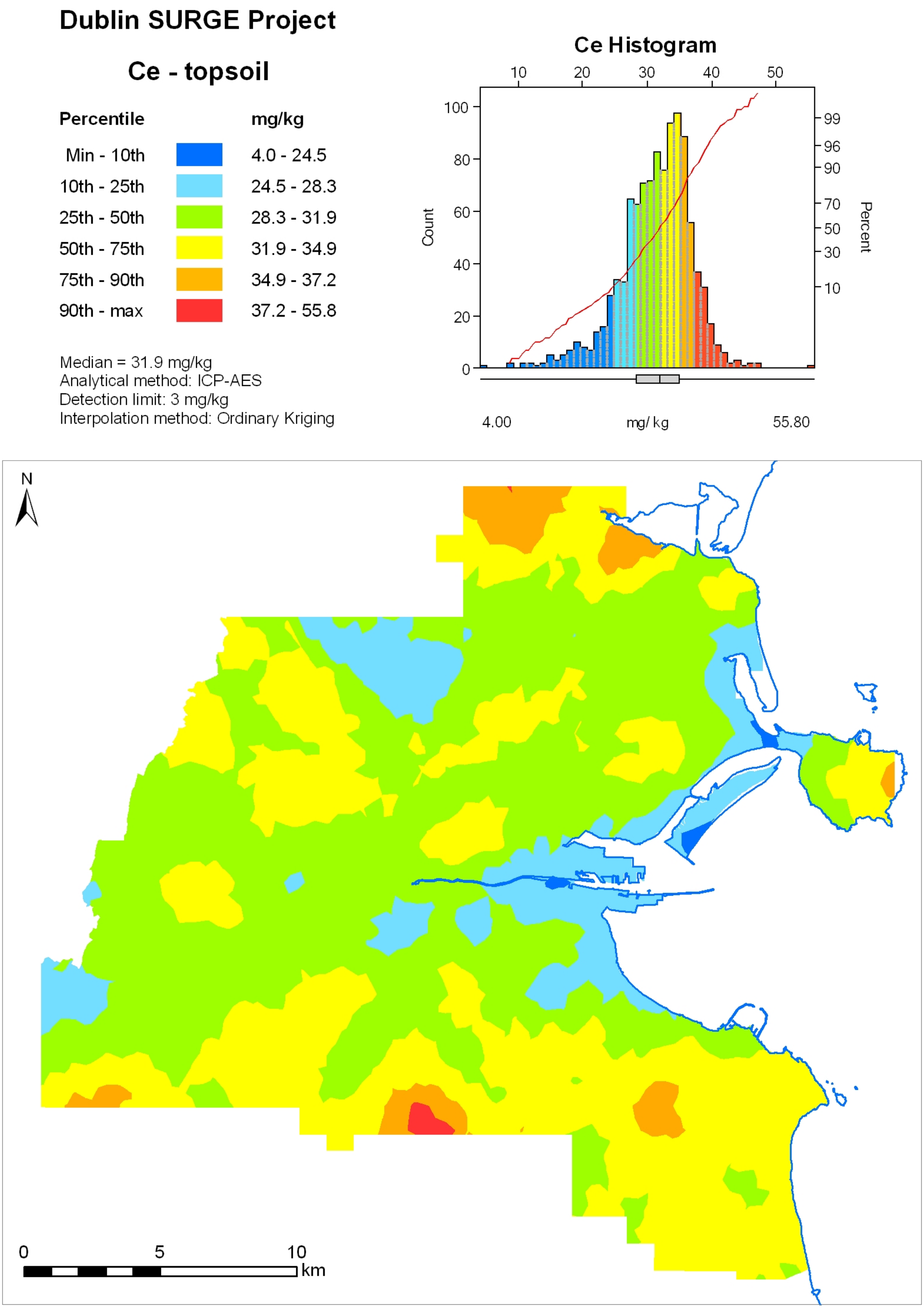


Figure 39 Topsoil Ce concentrations in the greater Dublin area

Iron – Fe

Iron is the fourth most abundant element and second most abundant metal in the Earth's crust (de Vos & Tarvainen, 2006). It is found in many common minerals, including pyrite, magnetite, haematite and siderite (de Vos & Tarvainen, 2006). Clays, shales and greywackes are generally enriched with Fe (>6%) compared to carbonate rocks (c.0.5%) (de Vos & Tarvainen, 2006). Iron is the most commonly used metal, mainly in alloys for the production of cast iron, wrought iron and steel (Fay *et al.,* 2007). Iron is an essential element for plants, animals and humans.

Iron concentrations were determined using ICP-AES, with a method detection limit of 4.5 mg/kg (0.00045%). Fe was detected at levels ranging from 0.31% to 5.48% with a median value of 2.21% in the greater Dublin area (Figure 40). Levels of Fe in rural soils in the greater Dublin area as measured in retested NSDB samples range between 1.1% to 2.79%.

Fe is relatively depleted in coastal areas. Fe concentrations over the 90th percentile level occur in association with impure limestones in the west and north of the survey area, and with shales and greywackes in southwest Dublin. The survey maximum value of Fe occurs in Dublin port, in a localised area of Fe enrichment possibly associated with human activities. The spatial distribution of Fe closely resembles that of Al.

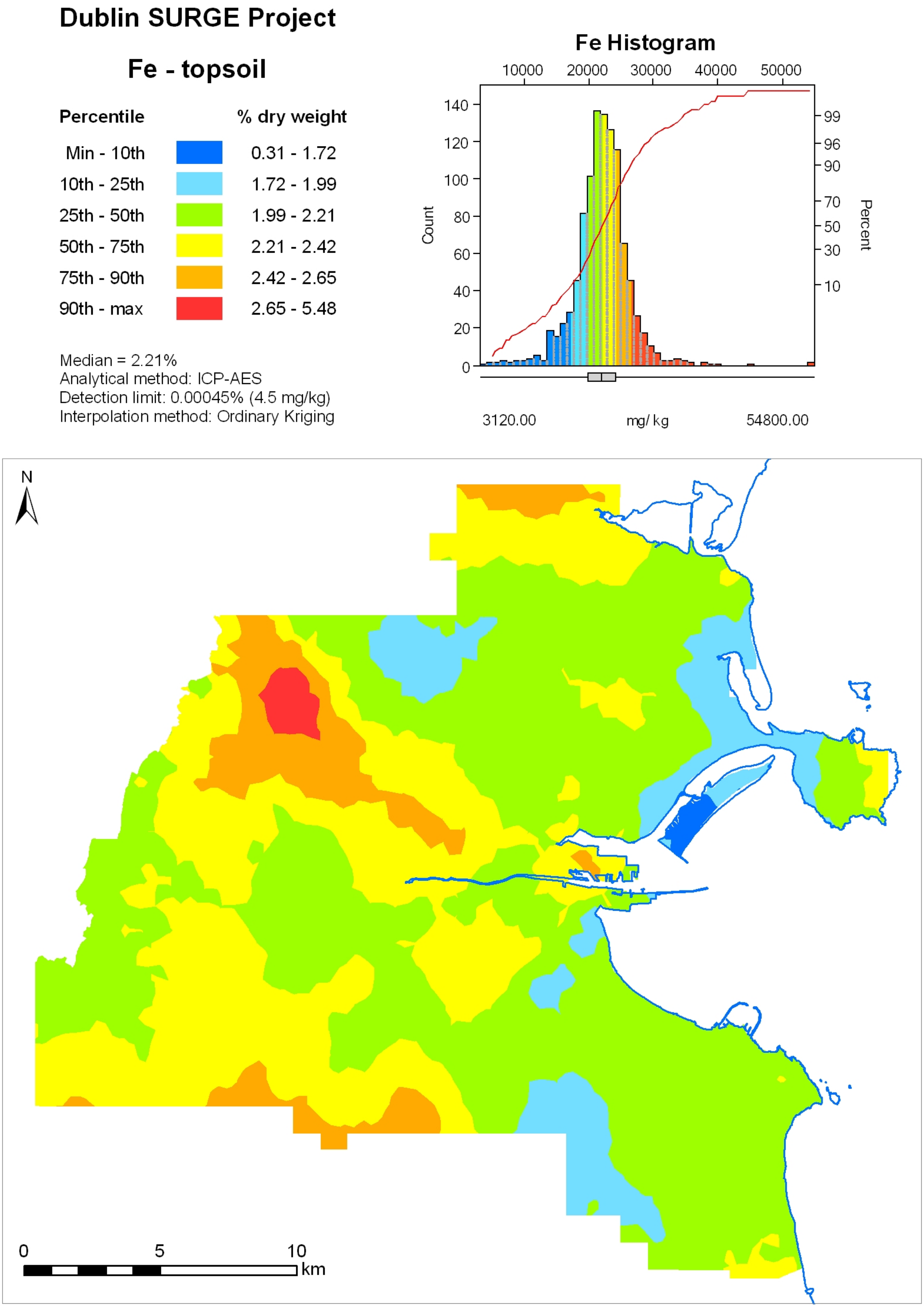


Figure 40 Topsoil Fe concentrations in the greater Dublin area

Potassium – K

Potassium is an alkali metal and is the eighth most abundant element in the earth's crust (de Vos and Tarvainen, 2006). Potassium is a constituent of many major rock-forming minerals such as alkali feldspar, biotite and muscovite (de Vos and Tarvainen, 2006). Impure carbonates rocks such as limestone tend to have K concentrations up to 6% due to their clay contents (de Vos and Tarvainen, 2006). K has many uses including in fertilisers, glass, detergents, dyes and fireworks (Fay *et al.,* 2007).

Potassium concentrations were determined using ICP-AES, with a method detection limit of 150 mg/kg (0.015%). K was detected at levels ranging from 0.06% to 1.71% with a median value of 0.72% in the greater Dublin area (Figure 41). Levels of K in rural soils in the greater Dublin area as measured in retested NSDB samples range between 0.52% to 0.87%.

Topsoil overlying the Cambrian metasediments of Howth Head is enriched with K (median level of 1.09%) with a when compared with topsoil overlying other bedrock types. Potassium is relatively depleted in inner city and coastal areas. Potassium concentrations over the 90th percentile level occur in association with impure limestones in the west and north of the survey area, and with shales and greywackes in southwest Dublin.

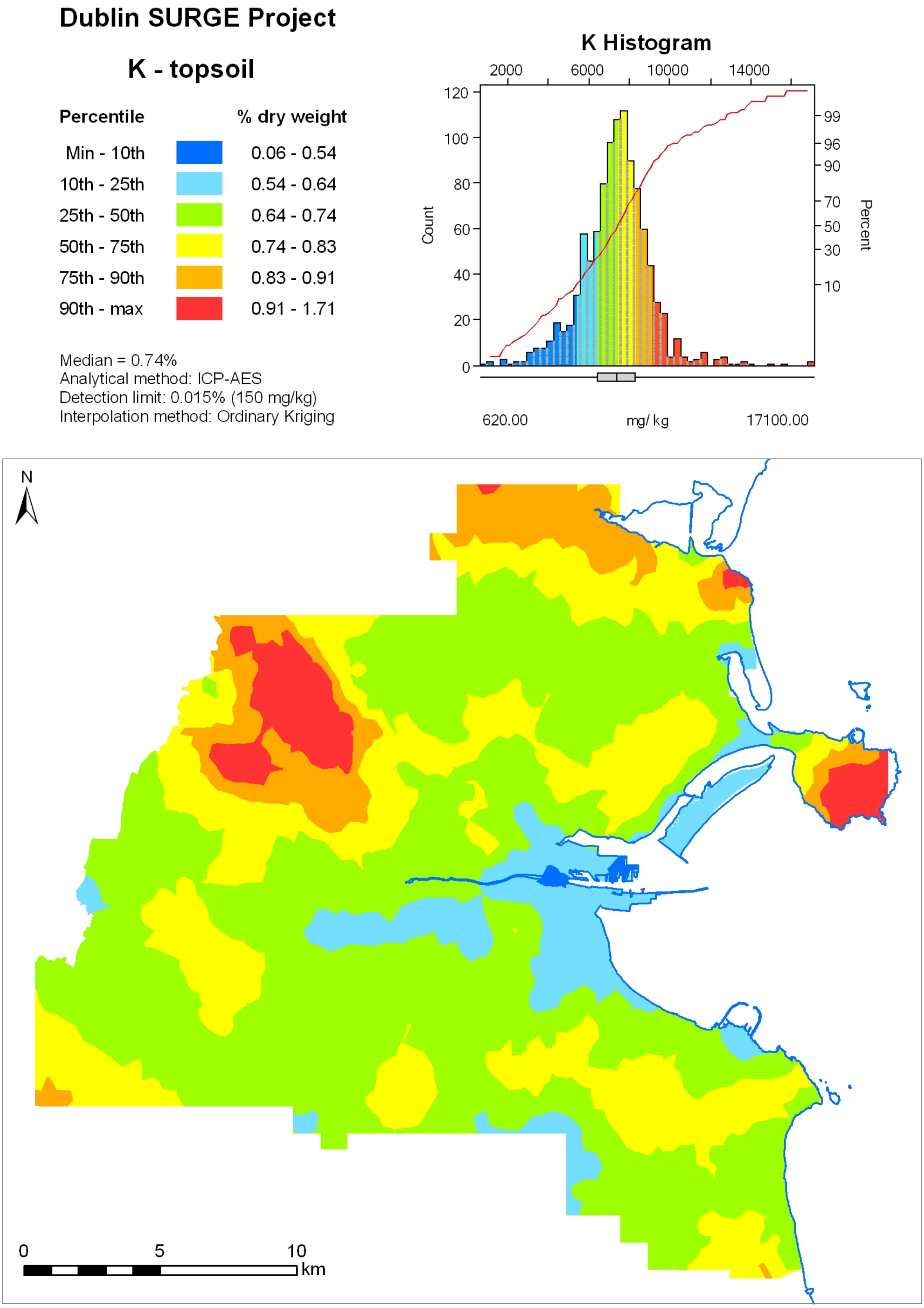


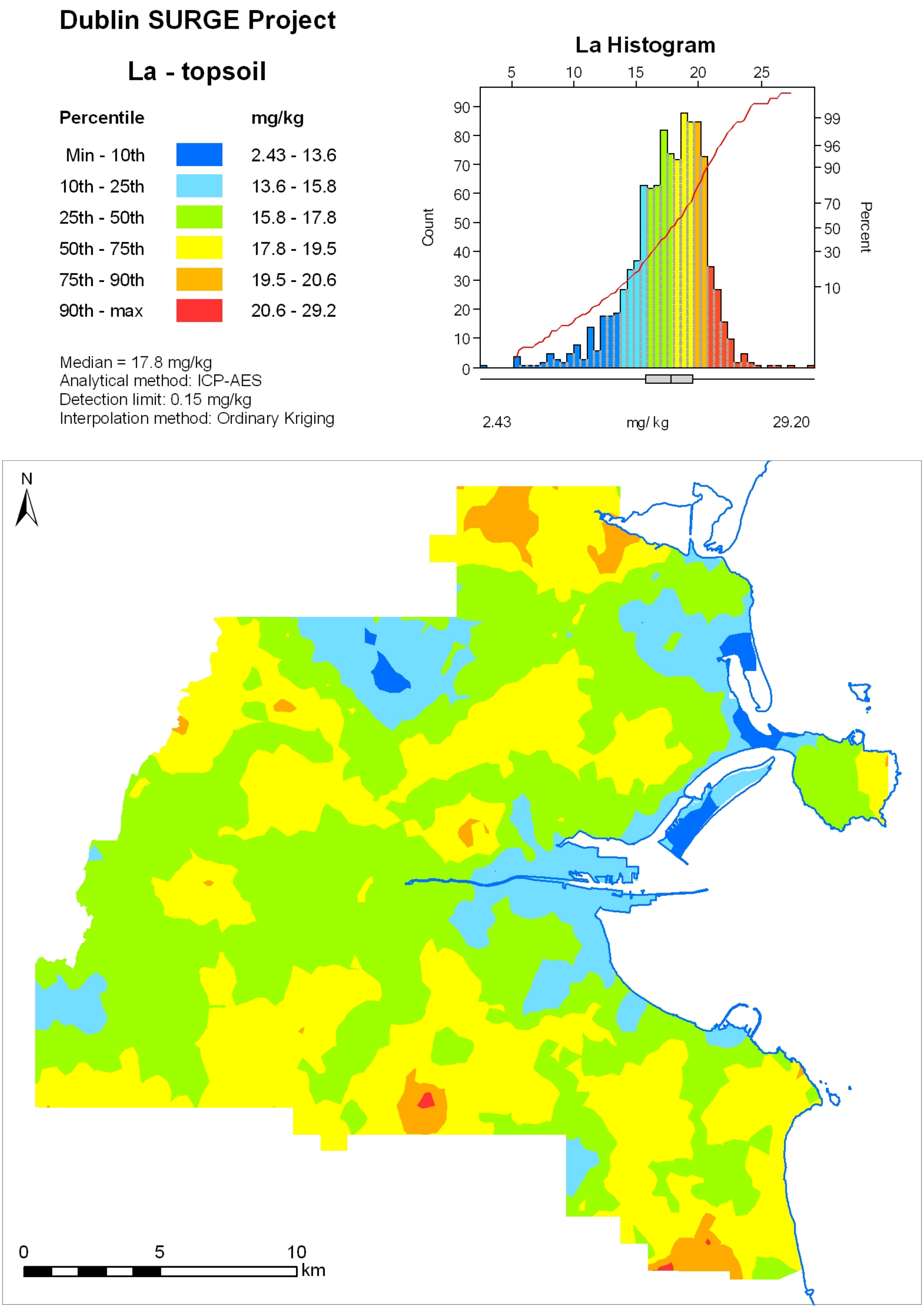
Figure 41 Topsoil K concentrations in the greater Dublin area

Lanthanum – La

Lanthanum is a rare earth metal which occurs in the minerals monazite and cerite and as a trace element in rock-forming minerals such as feldspar and pyroxene (de Vos and Tarvainen, 2006). Lanthanum content in limestone is generally low and mostly associated with impurities in the rock. It is more abundant in granitic, shale and greywacke rocks (de Vos and Tarvainen, 2006). Lanthanum is used commercially in lighting in the film industry, glass manufacturing and in petrol catalysts (Fay *et al.,* 2007).

Lanthanum concentrations were determined using ICP-AES, with a method detection limit of 0.15 mg/kg. Lanthanum was detected at levels ranging from 2.43 mg/kg to 29.2 mg/kg with a median value of 17.8 mg/kg in the greater Dublin area (Figure 42). Levels of La in rural soils in the greater Dublin area as measured in retested NSDB samples range between 16.1 mg/kg and 22.9 mg/kg.

The spatial distribution of La in topsoil in Dublin in very similar to that of Ce, the other rare earth metal measured in this study. Cerium and La have a Pearson correlation coefficient of 0.98, indicating a very strong relationship between the two elements. They are relatively depleted in inner city and coastal areas. La concentrations over the 90th percentile level occur in association with the Leinster Granites in south Co. Dublin. Other areas of La enrichment occur in west and north Dublin possibly with impure limestones in the Dublin Basin area.



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La - topsoil

Percentile		mg/kg
Min - 10th	🟦	2.43 - 13.6
10th - 25th	🟦	13.6 - 15.8
25th - 50th	🟩	15.8 - 17.8
50th - 75th	🟨	17.8 - 19.5
75th - 90th	🟧	19.5 - 20.6
90th - max	🟥	20.6 - 29.2

Median = 17.8 mg/kg
Analytical method: ICP-AES
Detection limit: 0.15 mg/kg
Interpolation method: Ordinary Kriging

Figure 42 Topsoil La concentrations in the greater Dublin area

Lithium – Li

Lithium is a light, silver white metal which is a member of the alkali metal group of elements. Lithium is used commercially in lighting in the rechargeable batteries, alloys, lubricants, and in mood-stabilising medicines (Fay *et al.,* 2007).

Lithium concentrations were determined using ICP-AES, with a method detection limit of 0.75 mg/kg. Lithium was detected at levels ranging from 2.3 mg/kg to 128 mg/kg with a median value of 28.4 mg/kg in the greater Dublin area (Figure 43). Levels of Li in rural soils in the greater Dublin area as measured in retested NSDB samples range between 24.7 mg/kg and 132 mg/kg.

The Soil Geochemical Atlas of Ireland (Fay *et al.,* 2007) notes naturally elevated concentrations of Li in topsoil (>40 mg/kg) in the Leinster Granite region. This trend was also noted by O'Connor and Reimann (1993) in a regional stream sediment reconnaissance survey in the area. The study determined that Li was predominantly held in mica and spodumene minerals in the northern Leinster granite pluton and that the metasediments of the Ribband Group, which flank the northern pluton, have medium to high levels of Li.

The spatial distribution of La in topsoil in Dublin is strongly correlated to the Leinster Granite batholith and associated metasediments in the south of the study area. Concentrations above the 90th percentile level for Li are widespread in this area. Other more localised Li anomalies are associated with the Calp. Li concentrations are depleted in Couceyan limestone units in the northern Dublin area.

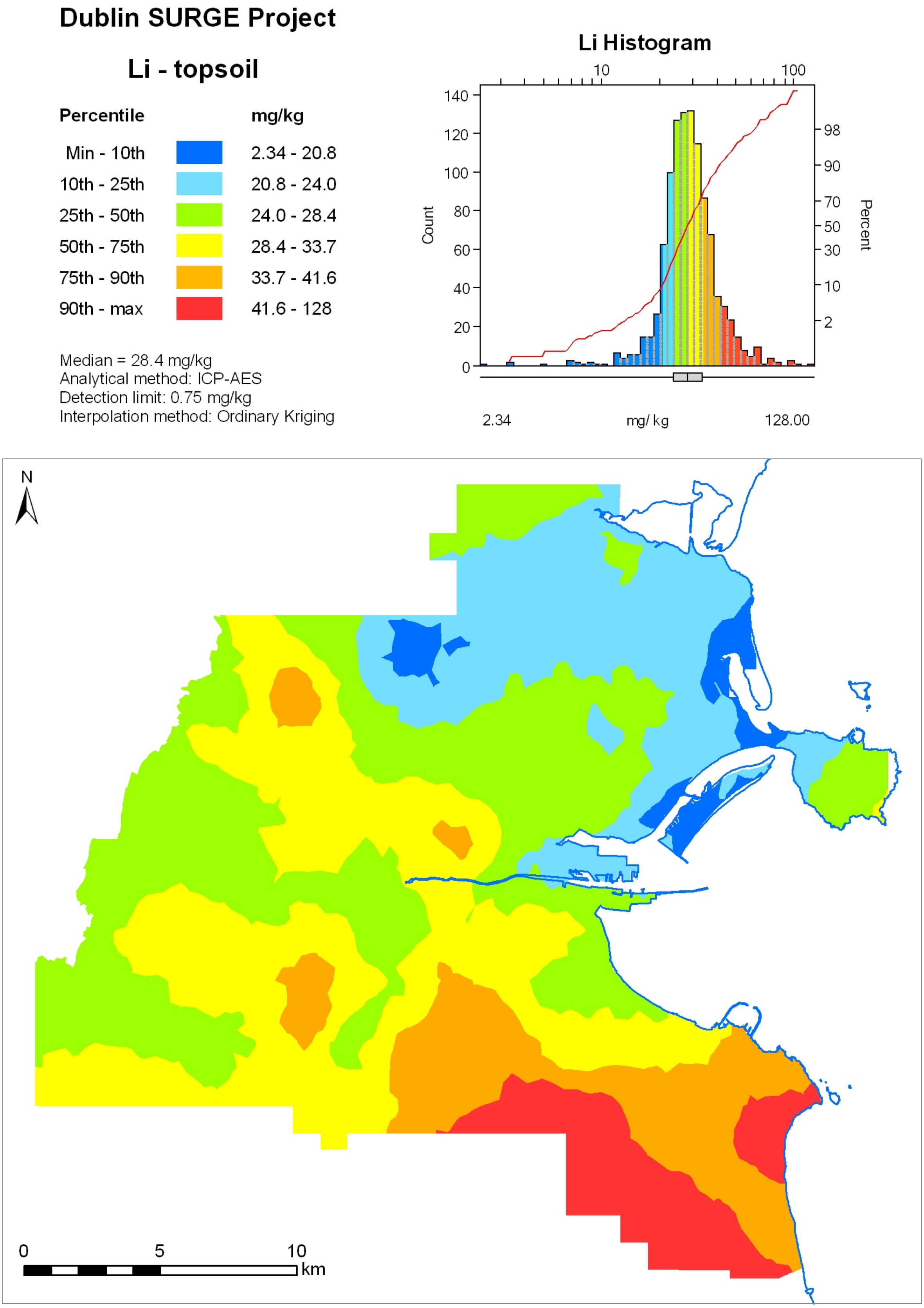

Figure 43 Topsoil Li concentrations in the greater Dublin area

Magnesium – Mg

Magnesium is a silvery white alkaline metal and is the seventh most abundant element in the earth's crust. It is an important component of many rock-forming silicate and carbonate minerals and has a high concentration in seawater (Wedepohl, 1983). Magnesium metal is used in alloys and Mg compounds are used in dessicants, fireworks, disinfectants and medicines (Fay *et al.,* 2007). Magnesium is an essential element for living organisms (Fay *et al.,* 2007).

Magnesium concentrations were determined using ICP-AES, with a method detection limit of 0.015%. Mg was detected at levels ranging from 0.07% to 12% with a median value of 0.43% in the greater Dublin area (Figure 44). Levels of Mg in rural soils in the greater Dublin area as measured in retested NSDB samples range between 0.22% and 0.5%.

Concentrations of Mg over the 90th percentile level occur in the north, west and southwest of the study area and in the inner city. The three highest concentrations of Mg occur in the city centre, where there may be an influence of human activities on Mg levels. Several limestone formations in the greater Dublin area are dolomitised (McConnell, 1994), meaning that the Ca in calcite has been replaced by Mg. This may account for localised enrichments of Mg in topsoil overlying limestone. Magnesium is also associated with dolerites in the Leinster Granites and with chlorite in the greywackes of southern Co. Dublin.

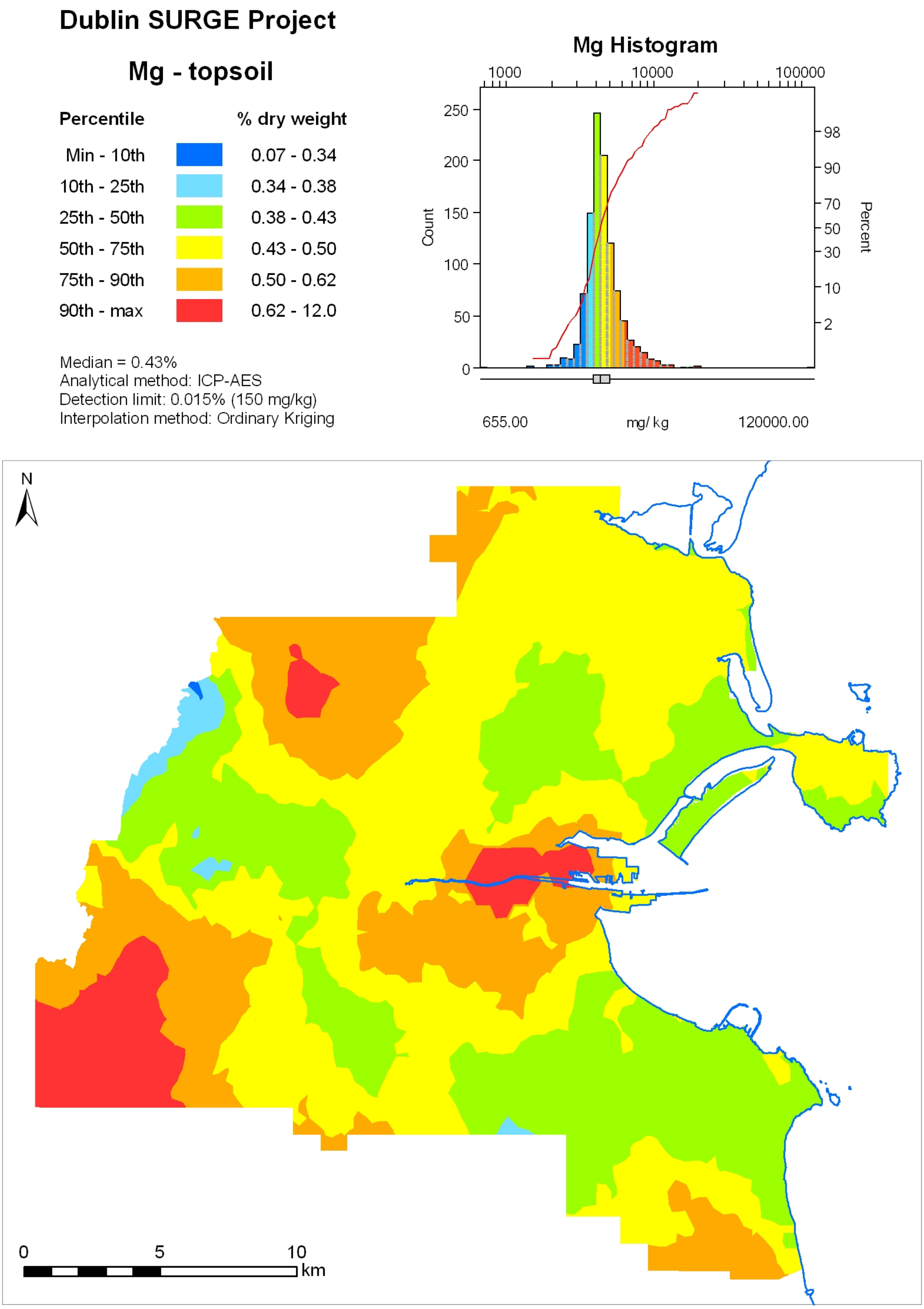

Figure 44 Topsoil Mg concentrations in the greater Dublin area

Manganese – Mn

Manganese is a relatively abundant metal which is found in nature in oxide, carbonate and silicate minerals (ATSDR, 2008d). It is used in steel, batteries, glass, fireworks, pigments and fertilisers (ATSDR, 2008d). Manganese is an essential element for living organisms (Fay *et al.,* 2007).

Manganese concentrations were determined using ICP-AES, with a method detection limit of 7.5 mg/kg. Manganese was detected at levels ranging from 89 mg/kg to 5,640 mg/kg with a median value of 946 mg/kg in the greater Dublin area (Figure 45). Levels of Mn in rural soils in the greater Dublin area as measured in retested NSDB samples range between 427 mg/kg and 1,600 mg/kg.

Concentrations of Mn over the 90th percentile level occur in west Co. Dublin over impure limestones. Mangenese nodules or coticules are known to occur in the Calp. Although limestones usually contain approximately 550 mg/kg Mn, some can contain high concentrations, associated with the mobilisation of Mn under reducing conditions in the sedimentary environment (Wedepohl, 1983). Manganese enrichments in southeast Dublin are possibly associated with metalliferous mineralisation in and around the Leinster granites.

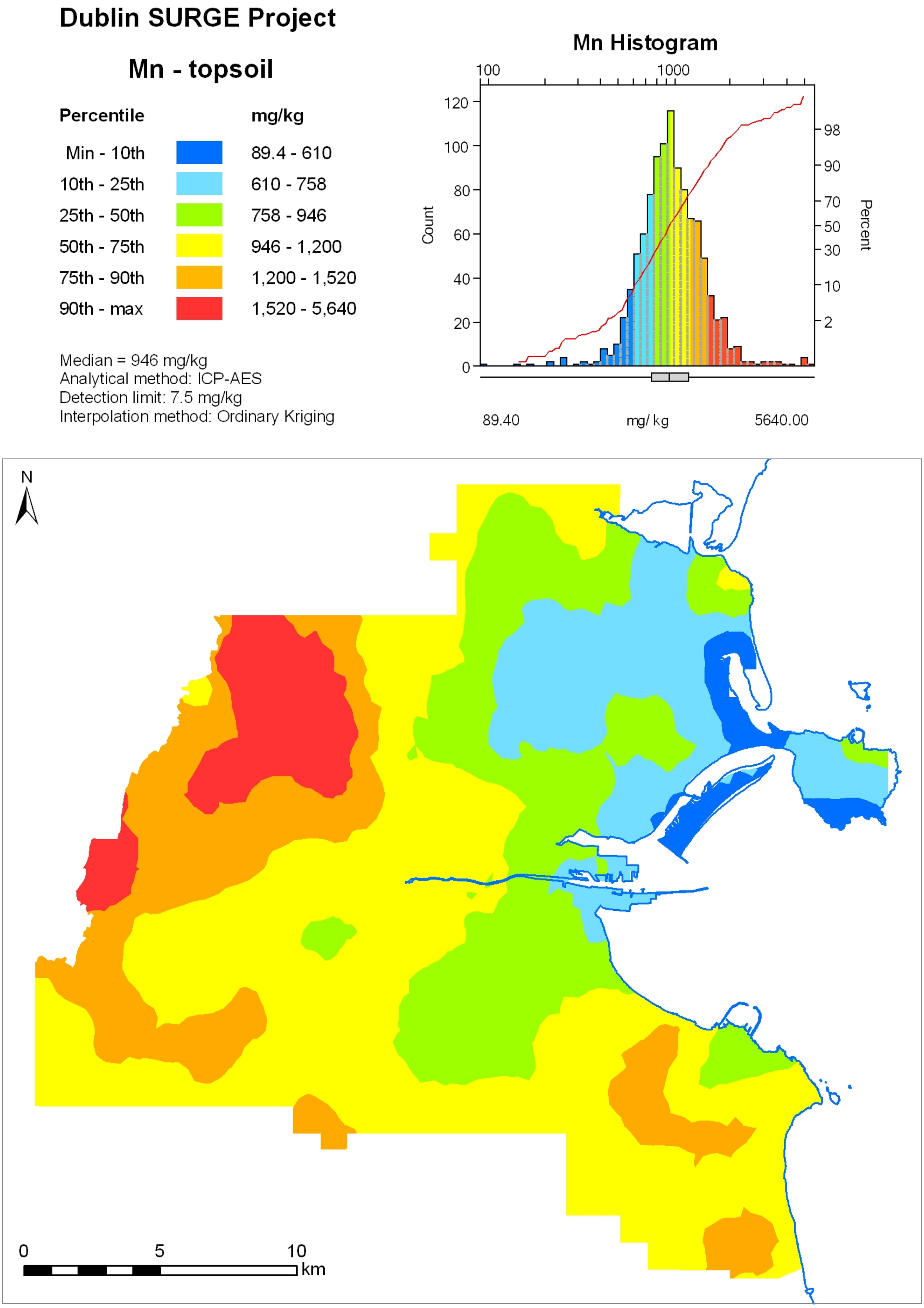

Figure 45 Topsoil Mn concentrations in the greater Dublin area.

Sodium – Na

Sodium is the most abundant alkali metal, the fifth most abundant element in the earth’s crust and the principle cation in seawater (de Vos and Tarvainen, 2006). Sodium forms a component of many major phosphate, halide, carbonate, nitrate and borate minerals (de Vos and Tarvainen, 2006). Sodium compounds are used in the paper, glass, soap, textile, petroleum, chemical and metal industries (de Vos and Tarvainen, 2006). Sodium is an essential element for animals and humans.

Sodium concentrations were determined using ICP-AES, with a method detection limit of 300 mg/kg. Sodium was detected at levels ranging from below the limit of detection to 2,460 mg/kg with a median value of 657 mg/kg in the greater Dublin area (Figure 46). Levels of Na in rural soils in the greater Dublin area as measured in retested NSDB samples range between 394 mg/kg and 680 mg/kg.

The highest concentrations of Na occur in topsoil overlying the limestones of the Dublin basin. These levels can be attributed to the presence of seawater during the formation of the limestone and clay minerals in shaly limestone (de Vos and Tarvainen, 2006). Concentrations above the 90th percentile level also occur in southeast Dublin, associated with the Leinster granites.

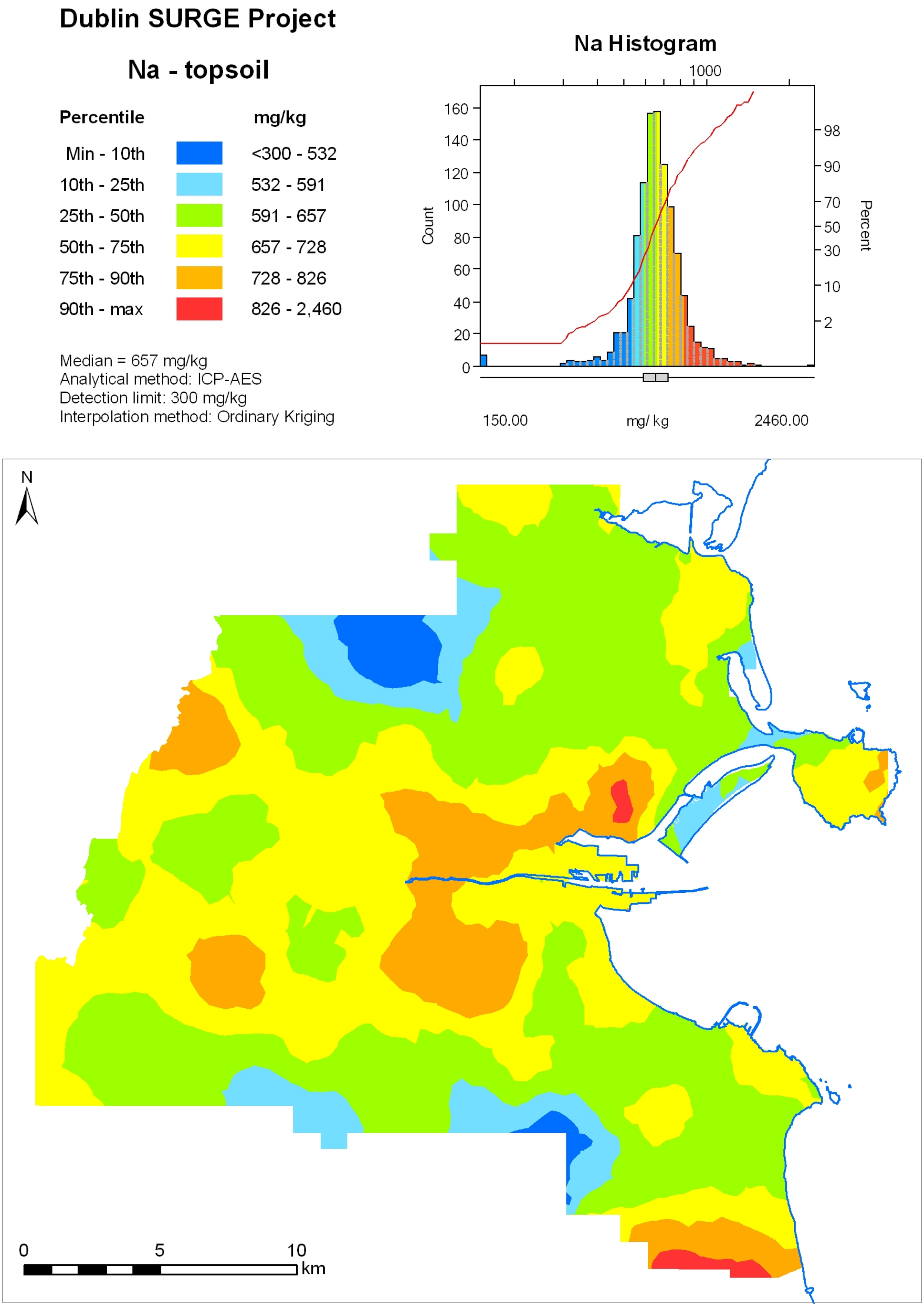

Figure 46 Topsoil Na concentrations in the greater Dublin area

Phosphorus – P

Phosphorus is a non-metallic inorganic element. It occurs mainly as orthophosphate in the mineral apatite but is widely dispersed at trace levels in many minerals and in biological materials such as bone (de Vos and Tarvainen, 2006). Most P is used commercially for fertiliser. It is also used in detergents, animal feed, metallurgical industry and food industry and as an additive to petroleum, insecticides and many other products (Wedepohl, 1983). Phosphorus is an essential element for all known forms of life (Fay *et al.,* 2007).

Phosphorus concentrations were determined using ICP-AES, with a method detection limit of 15 mg/kg. Phosphorus was detected at levels ranging from 165 mg/kg to 5,060 mg/kg with a median value of 984 mg/kg in the greater Dublin area (Figure 47). Levels of P in rural soils in the greater Dublin area as measured in retested NSDB samples range between 774 mg/kg and 1,420 mg/kg.

The highest concentrations of P occur in topsoil in inner city areas, with concentrations falling concentrically with distance from the city centre. This spatial distribution correlates well with that of the anthropogenic metals such as Hg, Pb and Cu and implies a diffuse atmospheric deposition source. This would suggest an anthropogenic influence on P concentrations in the greater Dublin area.

Historical industrial activities in the inner city which involved the use of P include match factories, artificial fertiliser factories and metalworks. There were at least three fertiliser factories in inner city Dublin in the 19th century an early 20th century which processed P, located at Alexandra Road (Dublin port), Sir John Rogerson's Quay and Cabra (Carrig, 2011). These areas are located within a zone of P concentrations above the 75th percentile level. Metalworks produced metal slag byproducts which can be high in phosphate (Breward and Albanese, in press).

In modern times crematoria may contribute to P in soils through atmospheric deposition. This is supported by the relatively strong correlation of P with Hg (Pearson correlation coefficient of 0.64). Another modern source of P in soils may be the use of P-based fertilisers in parks and open spaces.

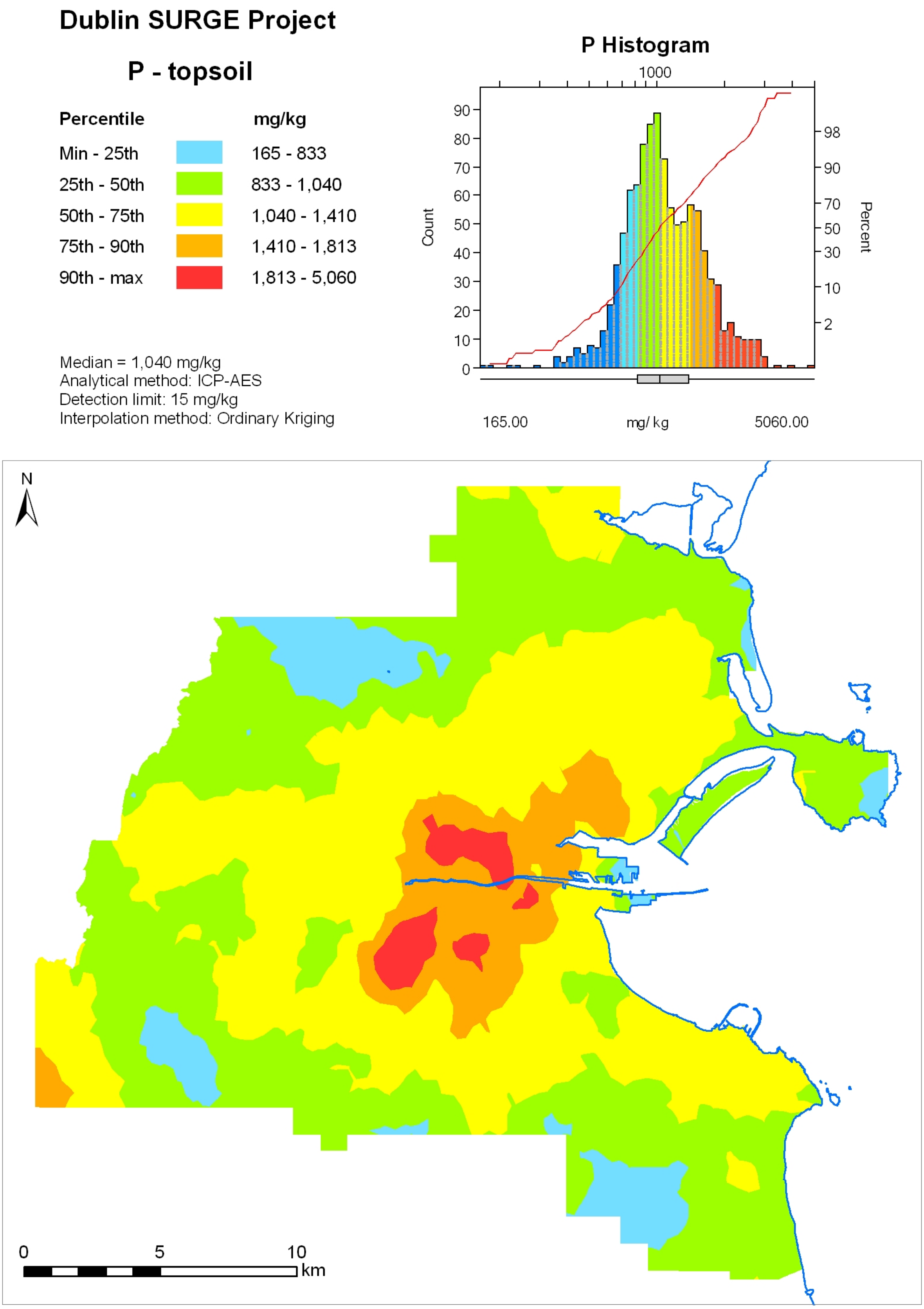

Figure 47 Topsoil P concentrations in the greater Dublin area

Scandium – Sc

Scandium is a rare metal which is usually only present in trace quantities in minerals (de Vos and Tarvainen, 2006). Sc is used in alloys, televisions, fluorescent lamps and energy-saving bulbs (de Vos and Tarvainen, 2006). Sc is not known to have any biological function (Fay *et al.,* 2007).

Scandium concentrations were determined using ICP-AES, with a method detection limit of 0.15 mg/kg. Scandium was detected at levels ranging from 0.2 mg/kg to 11.8 mg/kg with a median value of 6.12 mg/kg in the greater Dublin area (Figure 48). Levels of Sc in rural soils in the greater Dublin area as measured in retested NSDB samples range between 3.06 mg/kg and 8.63 mg/kg.

Scandium contents of sedimentary rocks are generally low. Limestones often contain <2 mg/kg Sc whereas argillaceous rocks have much higher concentrations, typically 10-30 mg/kg Sc (de Vos and Tarvainen, 2006). The range of values seen in this study probably reflects the high shale content in the impure limestones of the Dublin basin. Scandium is relatively depleted in coastal areas and in topsoil overlying the Leinster granites. Sc has very strong correlations with Al, Ce, Fe, La, V and Y.

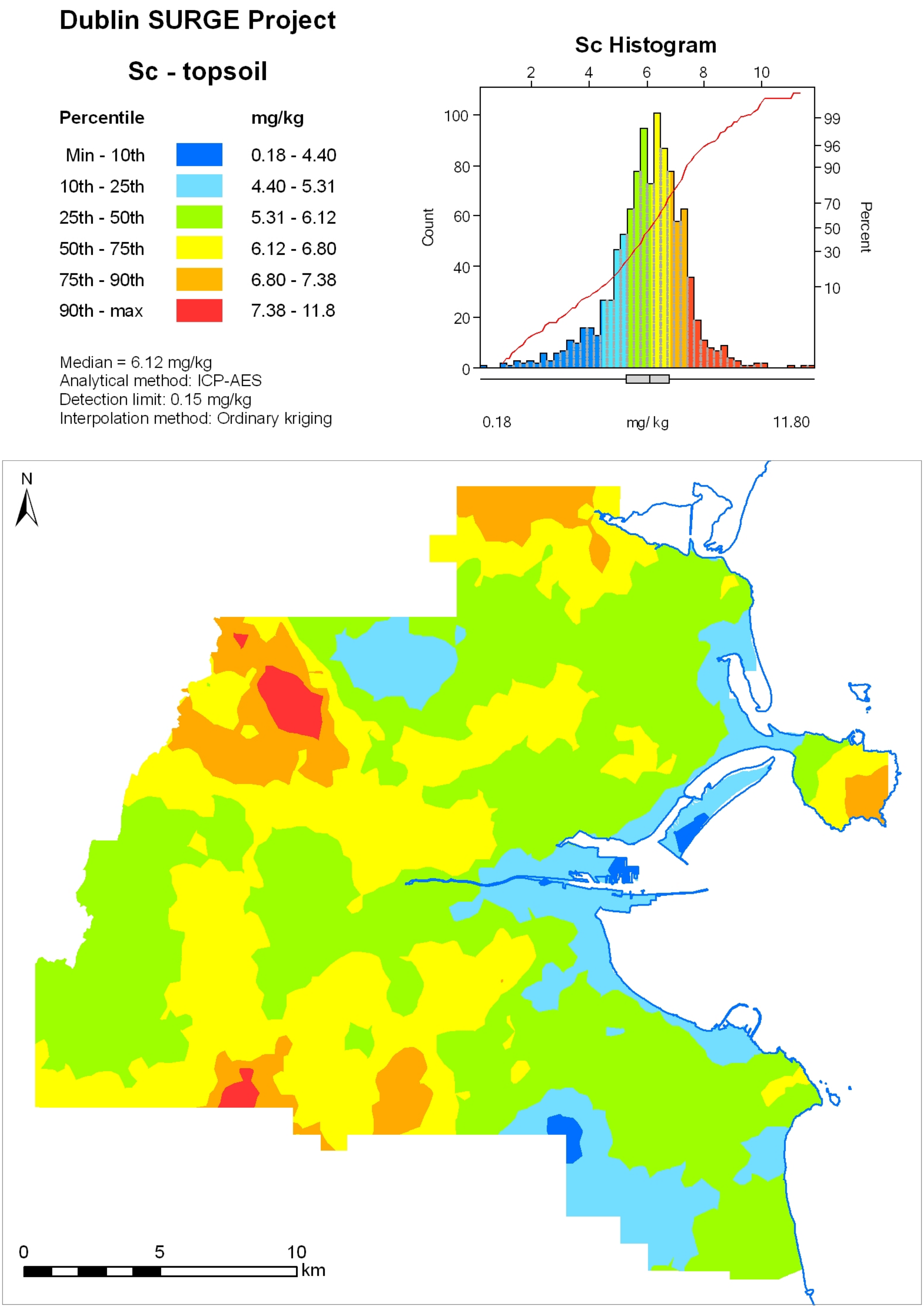

Figure 48 Topsoil Sc concentrations in the greater Dublin area

Strontium – Sr

Strontium is a hard, white coloured metal which is found in nature as several different Sr compounds (ATSDR, 2004c). Strontium compounds are used in making ceramics, glass, fireworks, pigments, fluorescent lights and medicines (ATSDR, 2004c). Sources of anthropogenic Sr contamination include metal refining, coal and incinerator ash disposal and radioactive Sr from nuclear tests (de Vos and Tarvainen, 2006). Radioactive Sr is produced artificially in nuclear reactors and weapons. Although its does not occur naturally, low levels of radioactive Sr occur worldwide due to nuclear activity. Exposure to radioactive Sr is harmful but the intake of radioactive Sr (mainly in food and water) for most people is likely to be very low (ATSDR, 2004c).

Strontium concentrations were determined using ICP-AES, with a method detection limit of 1.5 mg/kg. Strontium was detected at levels ranging from 11.5 mg/kg to 1,330 mg/kg with a median value of 127 mg/kg in the greater Dublin area (Figure 49). Levels of Sr in rural soils in the greater Dublin area as measured in retested NSDB samples range between 23.5 mg/kg and 139 mg/kg.

Strontium is chemically very similar to Ca and its spatial distribution in Dublin closely resembles that of Ca (Pearson correlation coefficient of 0.94). The substitution of Sr for Ca in carbonate minerals accounts for enrichments of up to 1,000 mg/kg Sr in limestones (de Vos and Tarvainen, 2006). Concentrations of Sr over the 90th percentile level occur in limestone areas in the Dublin basin area, in the centre, north and west of the study area, and is relatively depleted in topsoil overlying the Leinster Granites and Cambrian metasediments of Howth Head. There may be an anthropogenic influence on Sr levels in the city centre, due to historic coal burning and the disposal of coal ash.

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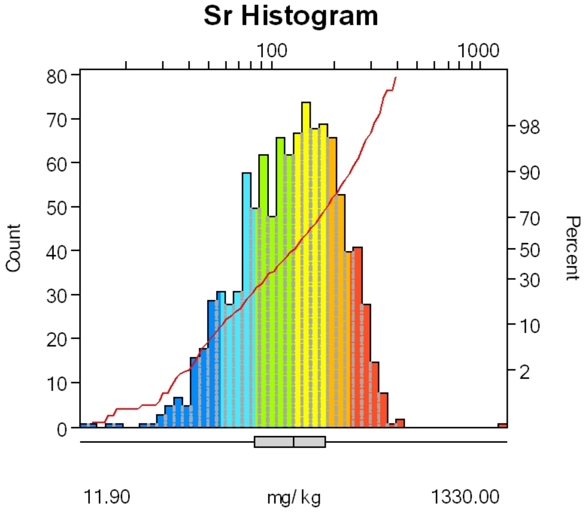
Sr - topsoil

Percentile		mg/kg
Min - 10th	🟦	11.9 - 56.2
10th - 25th	🟦	56.2 - 82.5
25th - 50th	🟩	82.5 - 127
50th - 75th	🟨	127 - 181
75th - 90th	🟧	181 - 235
90th - max	🟥	235 - 1,330

Median = 127 mg/kg
Analytical method: ICP-AES
Detection limit: 1.5 mg/kg
Interpolation method: Ordinary kriging



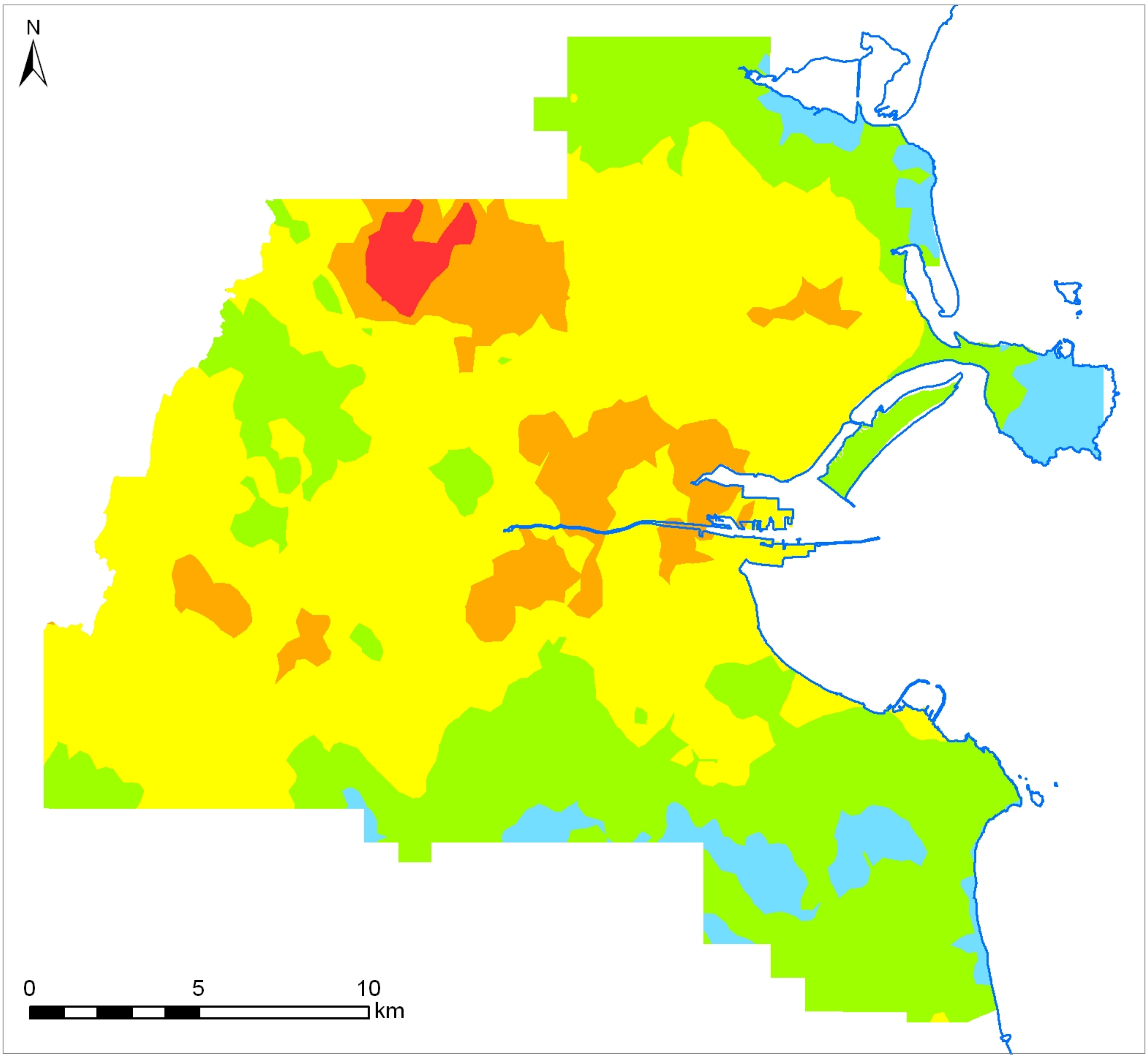


Figure 49 Topsoil Sr concentrations in the greater Dublin area

Titanium – Ti

Titanium is a lightweight, corrosion-resistant transition metal. It is relatively abundant in the earth's crust and forms several minerals, particularly in mafic (Fe and Mg-rich) igneous rocks (de Vos and Tarvainen, 2006). It is used in paint pigments, metal alloys for aircraft, ship and missile parts and in precision instruments (de Vos and Tarvainen, 2006).

Titanium concentrations were determined using ICP-AES, with a method detection limit of 1.5 mg/kg. Titanium was detected at levels ranging from 20.8 mg/kg to 575 mg/kg with a median value of 201 mg/kg in the greater Dublin area (Figure 50). Levels of Ti in rural soils in the greater Dublin area as measured in retested NSDB samples range between 156 mg/kg and 274 mg/kg.

Carbonate rocks such as limestone contain relatively little Ti (400-1,500 mg/kg) compared to felsic igneous rocks such as granite (c.2,000 mg/kg Ti) and shales and greywackes (<3,000 mg/kg Ti) (de Vos and Tarvainen, 2006). Topsoil overlying the Ordovician greywackes, sandstones and shales of south Dublin returned the highest median of the bedrock types at 250 mg/kg. However, the three highest Ti values were detected in inner city locations. Ti concentrations in this area are possibly influenced by anthropogenic activity such as coal burning and vehicle engine wear, but are still within the expected range of Ti concentrations for topsoil overlying limestones.

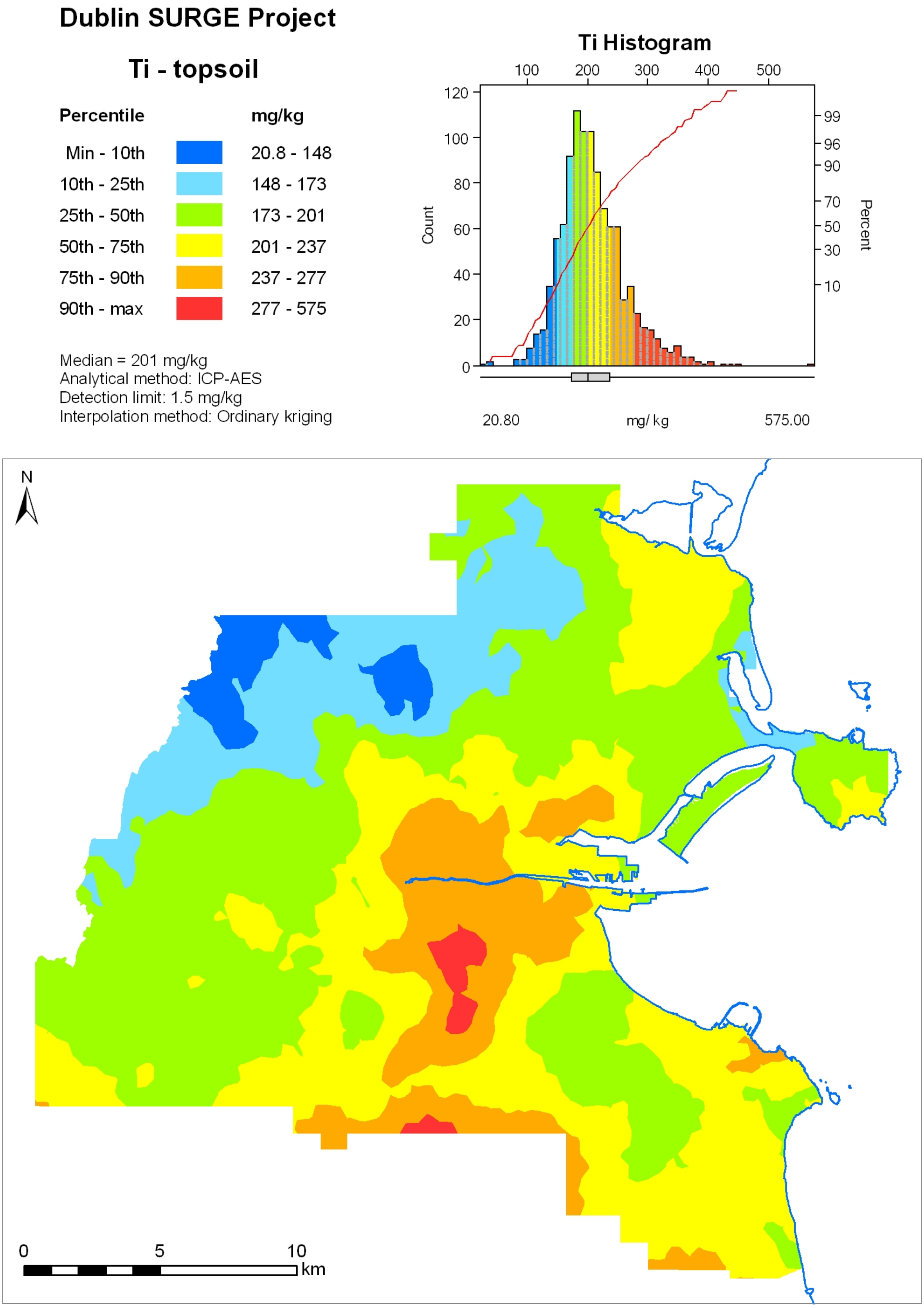


Figure 50 Topsoil Ti concentrations in the greater Dublin area

Yttrium - Y

Yttrium is a silvery white transition metal. It forms minerals such as xenotime and yttrialite and is a trace element in several others (de Vos and Tarvainen, 2006). It is used in alloys, spark plugs, fluorescent lamps, bulbs and in the production of catalysts and glass (de Vos and Tarvainen, 2006).

Yttrium concentrations were determined using ICP-AES, with a method detection limit of 0.1 mg/kg. Yttrium was detected at levels ranging from 2.4 mg/kg to 26.4 mg/kg with a median value of 14.3 mg/kg in the greater Dublin area (Figure 51). Levels of Y in rural soils in the greater Dublin area as measured in retested NSDB samples range between 8 mg/kg and 20 mg/kg.

Shales and greywackes are typically enriched with Y (>30 mg/kg) compared to carbonate rocks and sandstones (de Vos and Tarvainen, 2006). The range of values seen in this study probably reflects the high shale content in the impure limestones of the Dublin basin. Yttrium is relatively depleted in coastal areas and in topsoil overlying the Leinster granites. Y has strong to very strong correlations with Al, B, Ce, Co, Cr, Fe, K, La, Ni, Sc, and V.

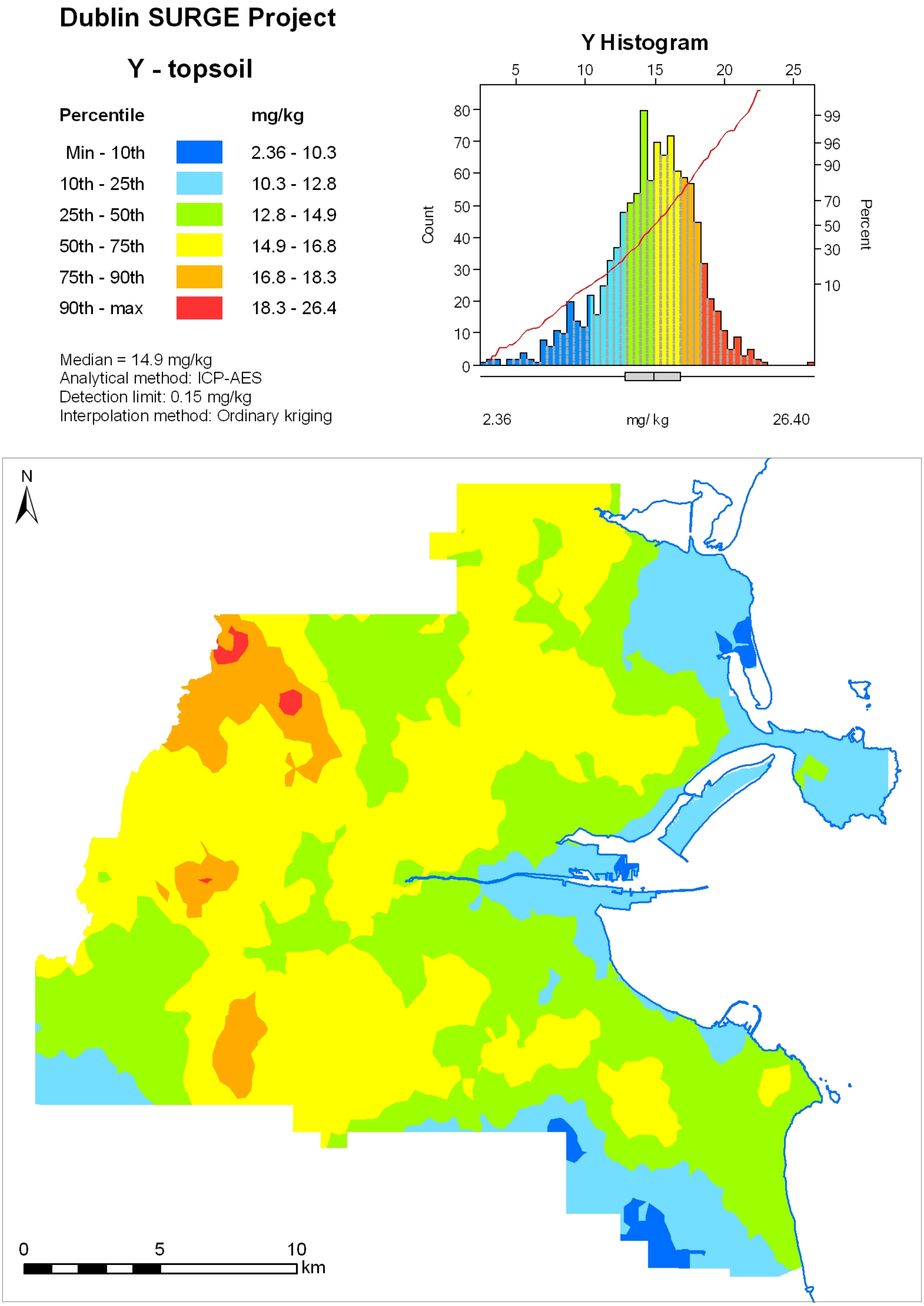


Figure 51 Topsoil Y concentrations in the greater Dublin area

Zirconium - Zr

Zirconium is a lustrous, grey-white transition metal. It forms several minerals including zircon (de Vos and Tarvainen, 2006). Most Zr metal is used in nuclear applications; other uses include alloys, catalytic converters, furnace bricks, laboratory and surgical equipment (de Vos and Tarvainen, 2006).

Zirconium concentrations were determined using ICP-AES, with a method detection limit of 3 mg/kg. Zirconium was detected at levels ranging from below the limit of detection to 21.1 mg/kg with a median value of 12.9 mg/kg in the greater Dublin area (Figure 52). Levels of Zr in rural soils in the greater Dublin area as measured in retested NSDB samples range between 12.7 mg/kg and 16.1 mg/kg.

The concentrations of Zr in topsoils observed in this study are relatively low. The highest concentrations of Zr in topsoils (>15.5 mg/kg) in occur predominantly in the south, overlying the Leinster granites and surrounding metasediments. McConnell (1994) notes zircon occurrences in several varieties of the Leinster granites. South of the study area in the vicinity of Avoca, Co. Wicklow a natural Zr anomaly (>1000 mg/kg) occurs in association with volcanic lithologies (rhyolite and tuff) in that region (O'Connor and Reimann, 1993). Zirconium is relatively depleted in coastal and inner city areas, except for the survey maximum, which occurs in the Dublin Port area (21.1 mg/kg) and may be associated with industrial activities. Zirconium has strong correlations with Al, Ce, La and Sc.

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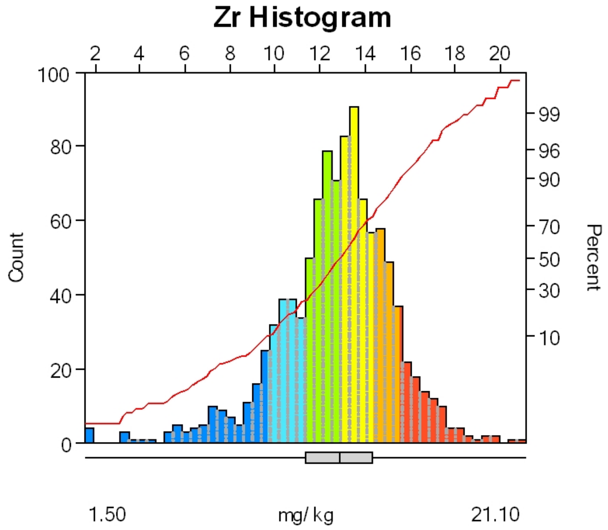
Zr - topsoil

Percentile		mg/kg
Min - 10th	🟦	<3 - 9.6
10th - 25th	🟦	9.6 - 11.3
25th - 50th	🟩	11.3 - 12.9
50th - 75th	🟨	12.9 - 14.3
75th - 90th	🟧	14.3 - 15.5
90th - max	🟥	15.5 - 21.1

Median = 12.9 mg/kg
Analytical method: ICP-AES
Detection limit: 3 mg/kg
Interpolation method: Ordinary kriging



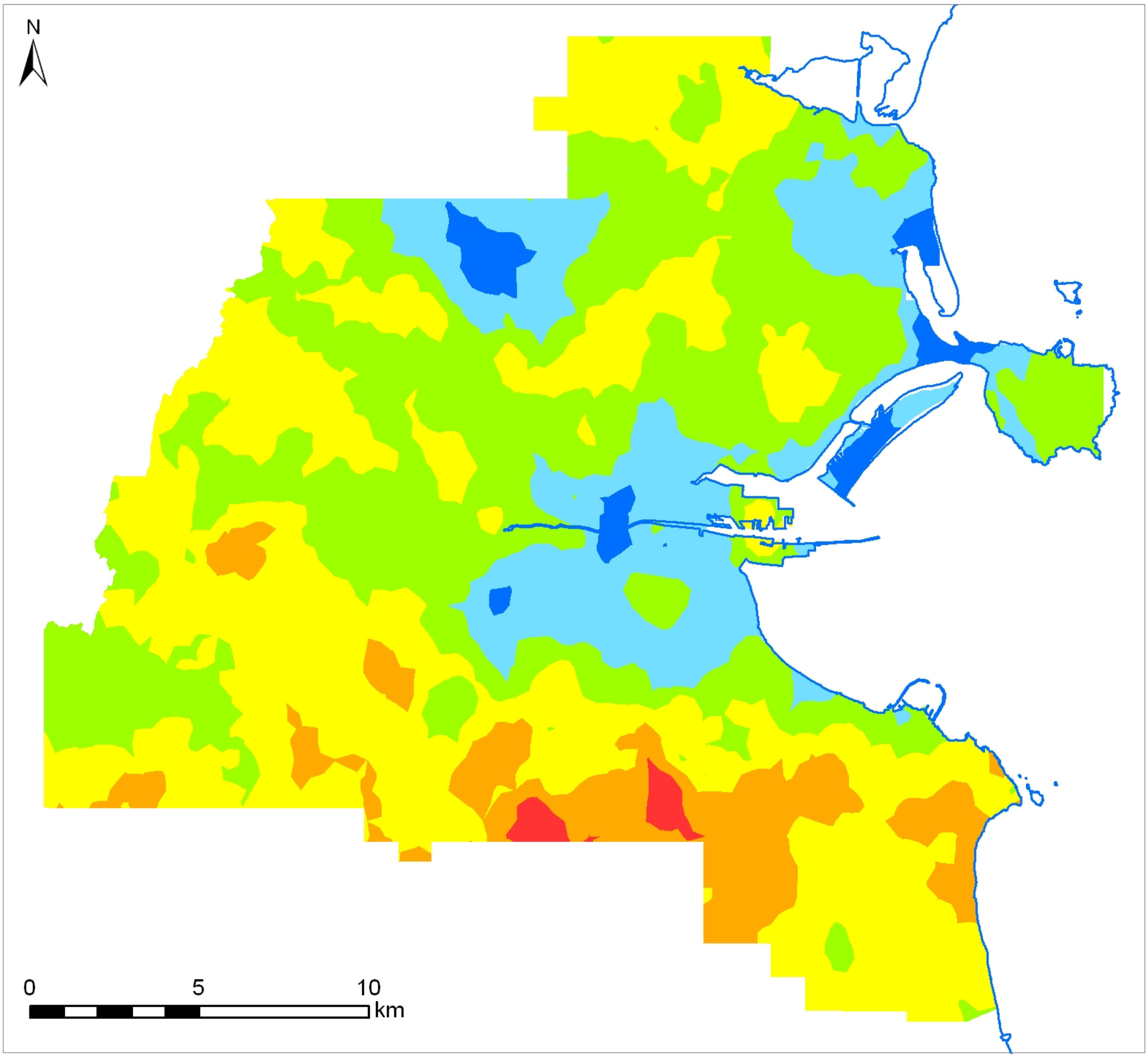


Figure 52 Topsoil Zr concentrations in the greater Dublin area

6.2 PAH Results

6.2.1 Basic statistics for the Greater Dublin Area

Basic statistics of minimum, maximum, mean, median and standard deviation for each PAH compound are given in Table 9. The sum of 16 PAHs (ΣPAH_{16}) was calculated by summing individual PAH compounds. Where individual compounds were not detected above the MDL, half of the MDL for each compound was used to conservatively approximate the sum. Half of the MDL was also used to represent samples less than the MDL in all the statistical calculations and assessments.

The percentage of samples with results less than the MDL are also listed for each analyte in Table 9. The LMW PAHs were not detected as frequently as the HMW PAHs. HMW PAHs tend to be more persistent in the environment as they are more resistant to bacterial, chemical or physical degradation than LWM PAHs. Table 9 shows that the lowest molecular weight PAHs of naphthalene, acenaphthylene, acenaphthene and fluorene were not detected in over half of the samples taken.

The maximum value measured for the sum of 16 PAHs was 661 mg/kg. At the same site maximum values were measured for all PAH compounds except naphthalene. The median value for the sum of 16 PAHs in the greater Dublin area was 3.47 mg/kg. A map of total 16 PAH compounds for the greater Dublin area shown in Figure 53. Maps for individual PAH compounds are shown in Appendix B.

	mg/kg dry weight					**% samples <MDL**
	Min	**Max**	**Mean**	**Median**	**St. Dev.**	
Naphthalene	<0.03	2.4	0.08	0.02	0.25	56.1
Acenaphthylene	<0.03	3.9	0.12	0.02	0.40	55.1
Acenaphthene	<0.03	17	0.21	0.02	1.26	58.2
Fluorene	<0.03	26	0.25	0.02	1.88	57.7
Anthracene	<0.03	50	0.56	0.06	3.65	38.3
Phenanthrene	<0.03	140	2.12	0.26	10.60	12.2
Fluoranthene	<0.03	130	3.28	0.55	10.74	5.1
Pyrene	<0.03	92	2.77	0.53	8.06	5.1
Benzo(a)anthracene	<0.03	51	1.58	0.29	4.61	13.3
Chrysene	<0.03	44	1.65	0.37	4.24	6.1
Benzo(a)pyrene	<0.03	28	1.15	0.26	2.86	10.7
Benzo(b)fluoranthene	<0.03	34	1.49	0.36	3.55	7.7
Benzo(k)fluoranthene	<0.03	14	0.53	0.12	1.35	20.4
Benzo(g,h,i)perylene	<0.03	14	0.78	0.22	1.72	11.2
Indeno(1,2,3-c,d)pyrene	<0.03	12	0.75	0.20	1.67	14.8
Dibenzo(a,h)anthracene	<0.03	4.4	0.20	0.05	0.48	41.8
ΣPAH_{16}	**0.24**	**661**	**17.52**	**3.47**	**55.17**	**5**

Table 9 Summary statistics for PAH results.

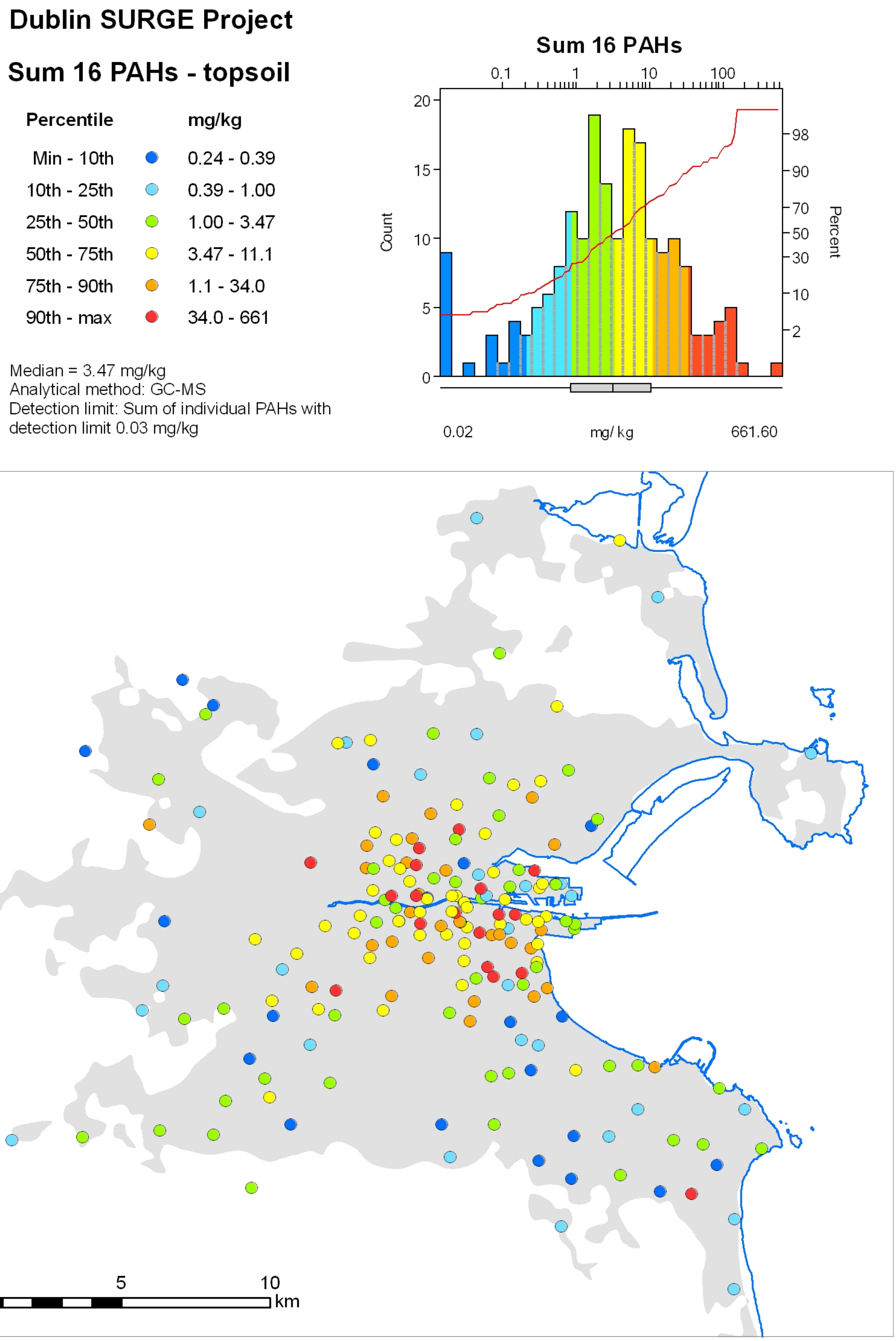


Figure 53 ΣPAHs$_{16}$ results for the greater Dublin area

6.2.2 Spatial distribution of PAHs

Boxplots were used to allow comparison of ΣPAH_{16} concentrations in different city zones (Figure 54). The City Centre zone registers the highest ΣPAH_{16} concentrations of the zones, with a median concentration of 5.94 mg/kg and a maximum value of 661.6 mg/kg. Median and maximum concentrations decline concentrically from the city centre through the Inner Suburban zone to the Outer Suburban zone. The Inner Suburban zone's median and maximum concentrations of ΣPAH_{16} are 4.91 mg/kg and 164 mg/kg respectively. Concentrations lower further in the Outer Suburban zone, with a median of 1.00 mg/kg and maximum of 89.7 mg/kg ΣPAH_{16}. The complete dataset for the whole city has a median of 3.47 mg/kg and a maximum value of 661 mg/kg. Three organic contaminant samples were taken in rural areas, but they were classed in the Outer Suburban zone due to their low number and proximity to urban areas.

Boxplots of individual PAH compounds for each city zone (Figure 55) show although the absolute concentrations of PAHs are highest in the City Centre zone, the overall composition of PAH compounds is similar across the zones. Each zone is dominated by the HMW PAHs, in particular fluoranthene and pyrene. PAH contamination from pyrogenic sources is believed to be characterised by the dominance of HMW PAHs (Banger *et al.,* 2010 and citations therein). Hence combustion is seen as the source of most PAHs in the greater Dublin area.

LWM PAH phenanthrene is also notably abundant,in the City Centre zone. Phenanthrene is the heaviest LWM PAH and is associated with both vapour and particulate phase transport in the atmosphere. ATSDR (1995a) notes that diesel exhaust particulates are dominated by the 3-4 ring PAH compounds of fluoranthene, phenanthrene and pyrene. These three compounds are the most abundant in the city centre zone and may reflect the stronger influence of traffic in the city centre over the outer city zones. Wind direction is dominantly easterly in Dublin, meaning that dispersion of contaminated particulates westwards over the city from industrial sources mainly in the docklands may have been limited somewhat. The absolute abundances of PAHs decline from the City Centre zone outwards, reflecting proximity to traffic and historical coal burning from domestic and industrial sources. In particular, higher abundances of LMW PAHs in the inner city indicate recent and active PAH emission sources.

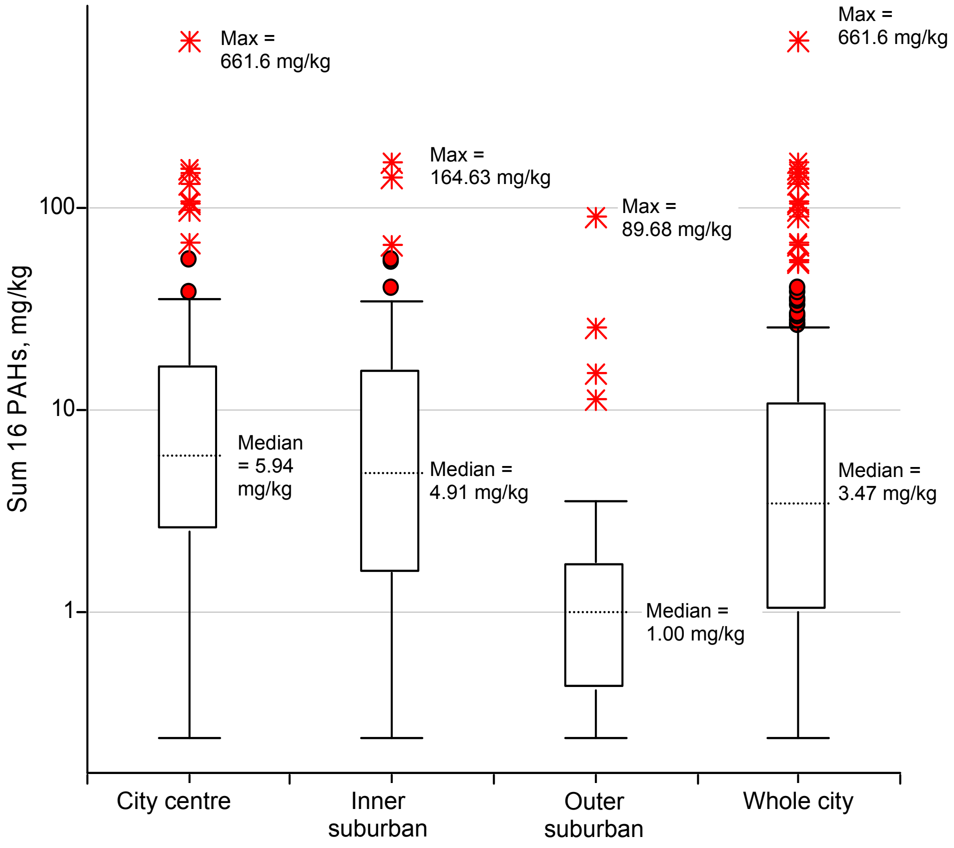
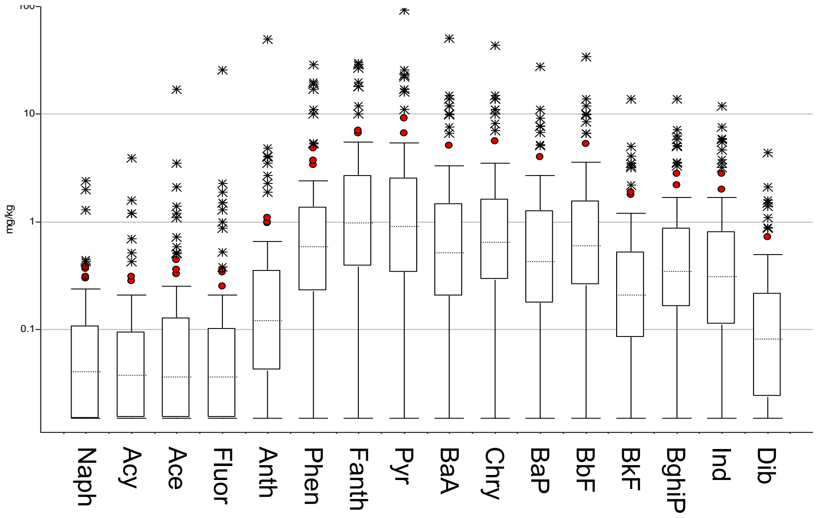
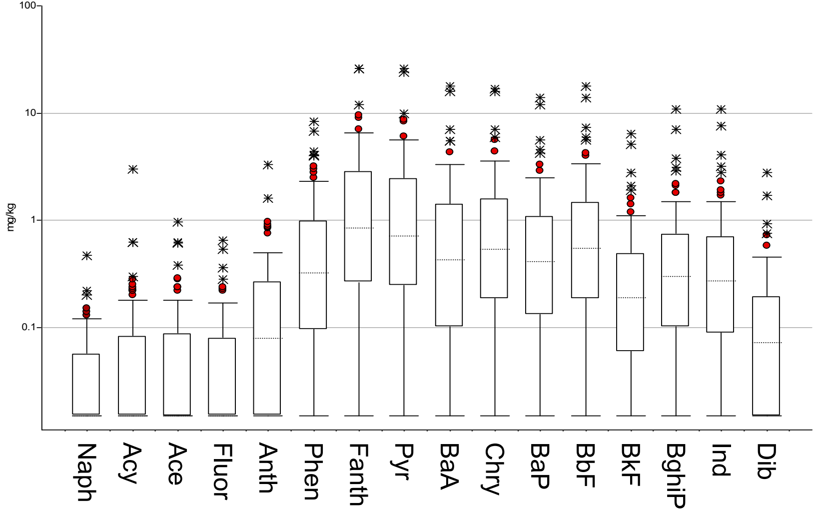


Figure 54 Boxplot for ΣPAH$_{16}$ in city zones

City Centre



Inner Suburban



Outer Suburban

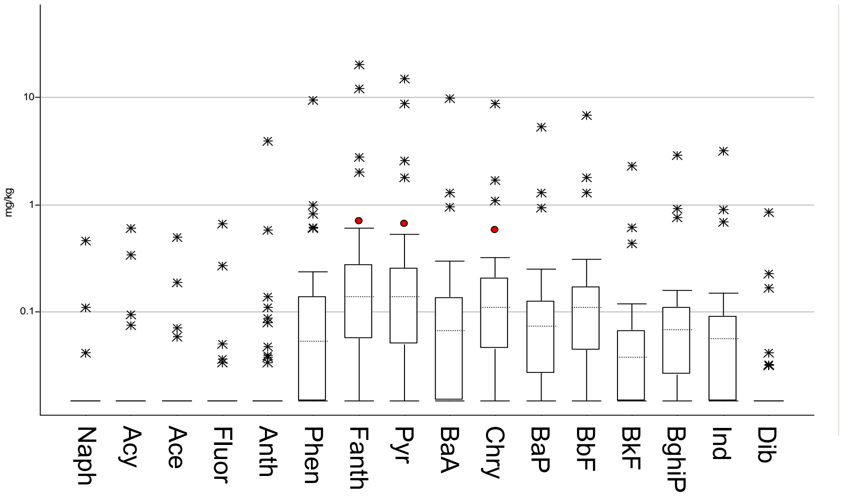


Figure 55 Individual PAH compound boxplots for city zones

6.3 PCB results

PCBs were detected at low levels at 14 sites in the greater Dublin area, which is just over 7% of all sites measured in the greater Dublin area (Figure 56 and Figure 57). PCBs were not detected above the limit of detection at other sites sampled.

6.3.1 Basic statistics and spatial distribution

Basic statistics for the PCB results are shown in Table 10. Due to high percentages of data below the limit of detection, medians could not be reliably calculated. The maximum level of ΣPCB_7 measured in the greater Dublin area was 0.0603 mg/kg. ΣPCB_7 was calculated by summing individual PCB congener results. Where individual compounds were below the MDL, half of the MDL for each compound was used to conservatively approximate the sum. With regard to multiple MDLs within one dataset, half of the overall lowest MDL was used to conservatively approximate the true numerical value for censored samples.

PCB congener no. 52 was not detected in the survey, while congener nos. 28 and 118 were detected rarely (once and twice respectively). Congener nos 101, 153 and 180 were detected more frequently and congener no. 138 was the most frequently detected, at 9 sites. The range of values detected for congener no. 138 was between 0.0033 mg/kg and 0.023 mg/kg.

Of the PCB detections, eight occurred in the City Centre zone and six occurred in the Inner Suburban zone. PCBs were not detected in the Outer Suburban zone.

	mg/kg dry weight		**% samples <MDL**
	Min	**Max**	
PCB Congener no. 28	<MDL	0.003	99%
PCB Congener no. 52	<MDL	<MDL	100%
PCB Congener no. 101	<MDL	0.0066	97%
PCB Congener no. 118	<MDL	0.0043	99%
PCB Congener no. 138	<MDL	0.023	95%
PCB Congener no. 153	<MDL	0.018	96%
PCB Congener no. 180	<MDL	0.019	97%
Sum 7 PCBs	**<MDL**	**0.0603**	**93%**

Table 10 Summary statistics for PCBs results

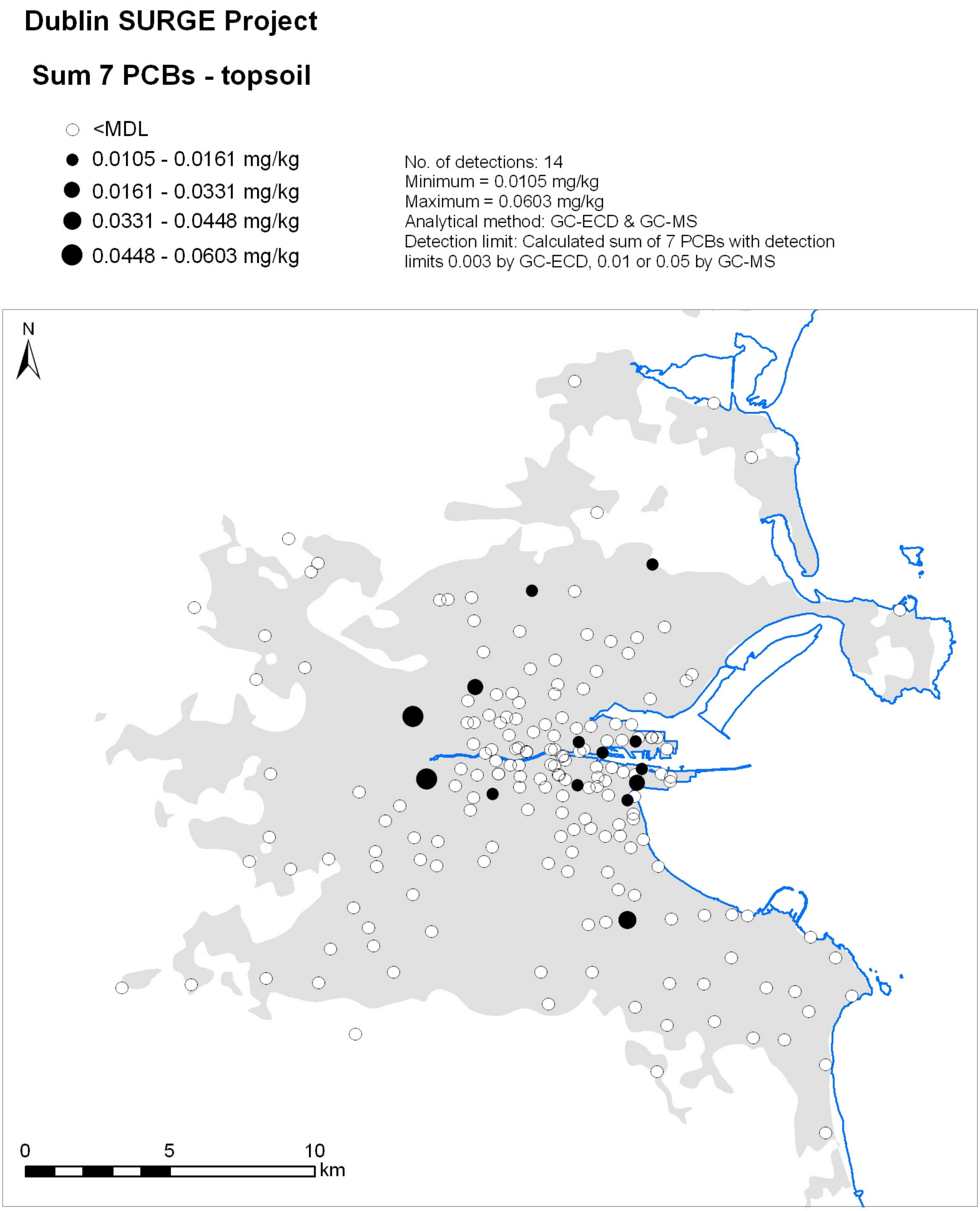
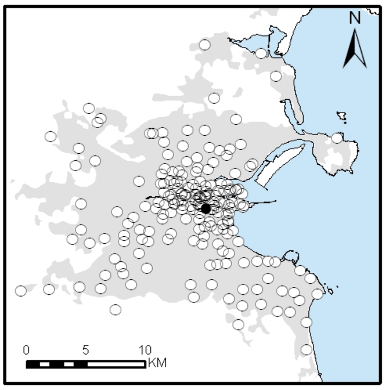


Figure 56 ΣPCB_7 for the greater Dublin area

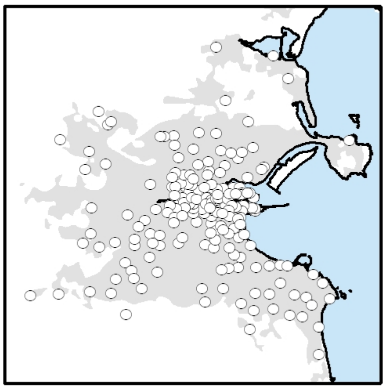
Dublin SURGE Project

Individual PCB Congeners - topsoil

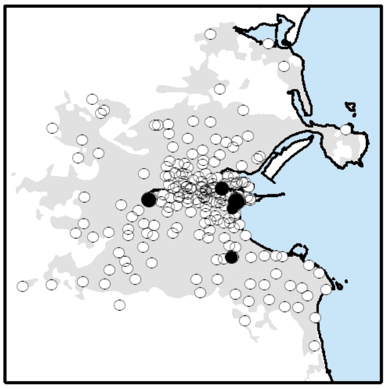
Analytical method: GC-ECD & GC-MS
Detection limits: 0.003 by GC-ECD
0.01 or 0.05 by GC-MS



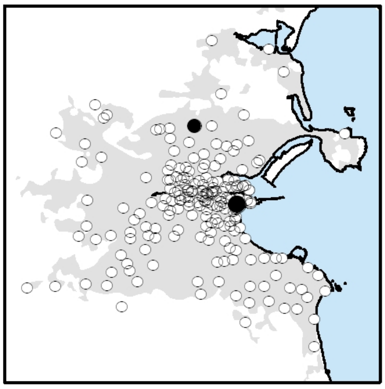
PCB Congener 28
mg/kg
○ <MDL ● 0.003



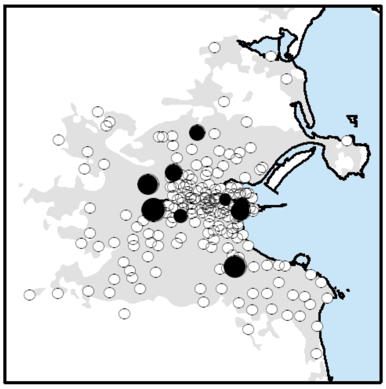
PCB Congener 52
mg/kg
○ < MDL



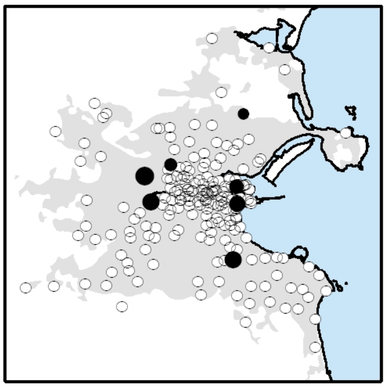
PCB Congener 101
mg/kg
○ <MDL ● 0.0033 ● 0.0058
● 0.0030 ● 0.0039 ● 0.0066



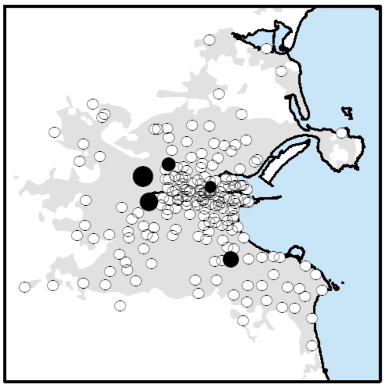
PCB Congener 118
mg/kg
○ <MDL
● 0.0035
● 0.0043



PCB Congener 138
mg/kg
○ <MDL ● 0.0040 ● 0.0110
● 0.0033 ● 0.0054 ● 0.0120
● 0.0035 ● 0.0057 ● 0.0230



PCB Congener 153
mg/kg
○ <MDL ● 0.0059 ● 0.0120
● 0.0038 ● 0.0071 ● 0.0140
● 0.0180



PCB Congener 180
mg/kg
○ <MDL ● 0.0049 ● 0.0130
● 0.0031 ● 0.0110 ● 0.0190

Figure 57 Individual PCB Congeners for the greater Dublin area

7 Discussion

7.1 Chemical Signatures

Analysing the compositions of inorganic elements and organic compounds in soil samples can provide valuable information on the potential sources of such substances in soil. In this section, inorganic elements including heavy metals are grouped together on the basis of their likely provenance. Although PAH and PCB compounds occur as complex mixtures, there are known chemical signatures for certain emission sources which can be compared to soil results to reveal likely emission sources.

7.1.1 Inorganic elements

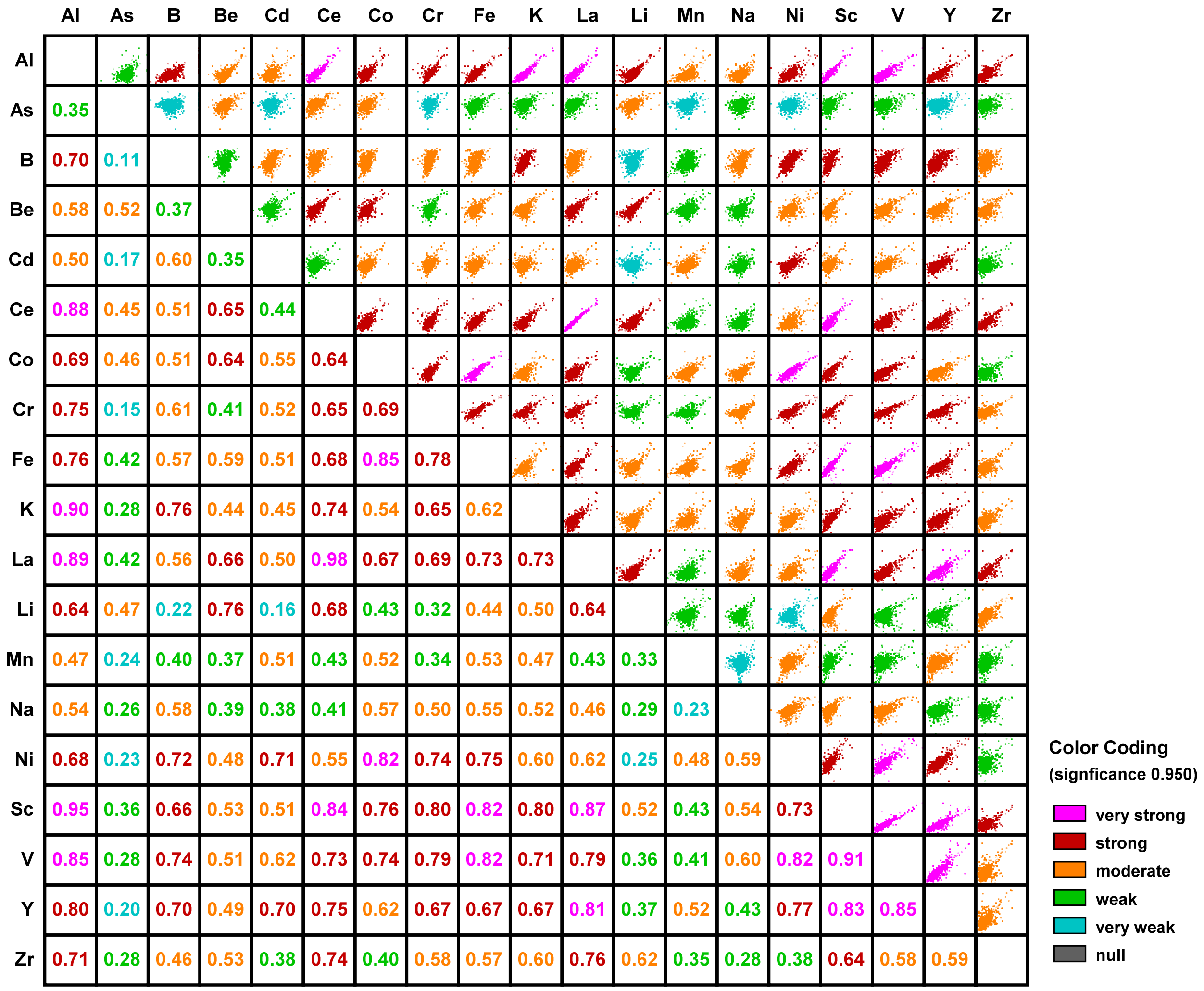
The relationships between inorganic elements were investigated using scatter plot matrices and by visually comparing the spatial distributions of elements. Three informal groups of inorganic elements were identified – an anthropogenic group, a geogenic group and a limestone group.

The geogenic group encompasses the elements Al, B, Be, Ce, Cr, Fe, K, La, Li, Sc, Y, V, Zr, and to a minor extent Cd, Mn, Na and As (Figure 58) These elements are characterised by naturally-derived enrichments occurring in the north and northwest of the survey area in the Dublin Basin. This is likely to be a sedimentary signature derived from impure Carboniferous limestones which are variably interbedded with shales and mudstones throughout the Dublin Basin.

Geogenic element concentrations are notably depleted in central and coastal areas. The predominance of made ground in the inner city and sandy soil types by the coast are likely to account for this trend. Made ground can be depleted in locally-derived geological materials compared to natural in-situ soils. Sandy soil types have low clay and organic matter contents, meaning that they are relatively depleted in clay minerals and have a low attenuation capacity for pollutants.

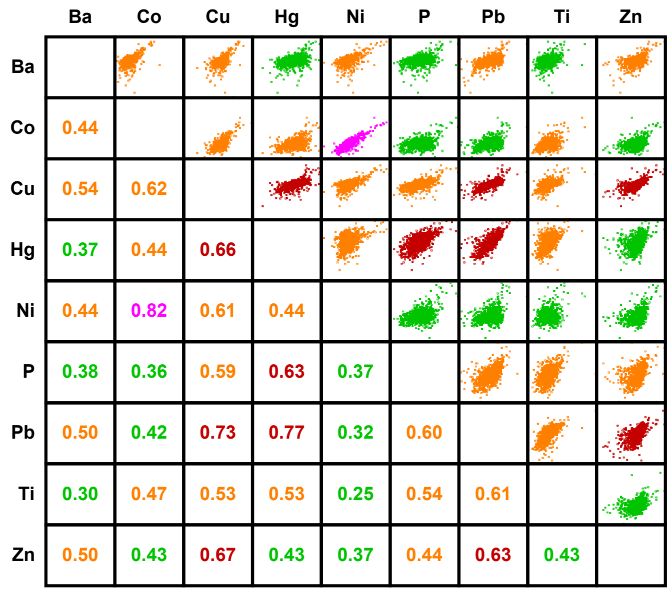
The anthropogenic group (Figure 60) is characterised by strong relationships between the occurrence of Pb, Cu, Hg and Zn, which show elevated concentrations in the inner city. Phosphorus, Ba and Ti also display this tendency to a lesser extent, with moderate correlations with the main anthropogenic metals. Elevated levels of the anthropogenic metals are consistent with Dublin's long history of habitation and industrial activity in the inner city and docklands areas. Potential sources of these metals include the coal industry (burning, storage, transportation and fly ash disposal), traffic (engine and tyre wear), industrial emissions, leaded petrol and paint.

The limestone group is characterised by the alkaline earth metals Ca, Sr and Mg in the Dublin basin limestone region (Figure 59).The occurrence and nature of Ca and Sr are closely related due to their similar chemical compositions. Limestone is primarily composed of calcite which is a Ca mineral. Both Sr and Mg can substitute for Ca in carbonate limestone minerals.

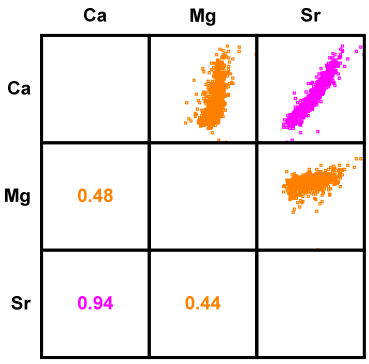


	Al	As	B	Be	Cd	Ce	Co	Cr	Fe	K	La	Li	Mn	Na	Ni	Sc	V	Y	Zr
Al																			
As	0.35																		
B	0.70	0.11																	
Be	0.58	0.52	0.37																
Cd	0.50	0.17	0.60	0.35															
Ce	0.88	0.45	0.51	0.65	0.44														
Co	0.69	0.46	0.51	0.64	0.55	0.64													
Cr	0.75	0.15	0.61	0.41	0.52	0.65	0.69												
Fe	0.76	0.42	0.57	0.59	0.51	0.68	0.85	0.78											
K	0.90	0.28	0.76	0.44	0.45	0.74	0.54	0.65	0.62										
La	0.89	0.42	0.56	0.66	0.50	0.98	0.67	0.69	0.73	0.73									
Li	0.64	0.47	0.22	0.76	0.16	0.68	0.43	0.32	0.44	0.50	0.64								
Mn	0.47	0.24	0.40	0.37	0.51	0.43	0.52	0.34	0.53	0.47	0.43	0.33							
Na	0.54	0.26	0.58	0.39	0.38	0.41	0.57	0.50	0.55	0.52	0.46	0.29	0.23						
Ni	0.68	0.23	0.72	0.48	0.71	0.55	0.82	0.74	0.75	0.60	0.62	0.25	0.48	0.59					
Sc	0.95	0.36	0.66	0.53	0.51	0.84	0.76	0.80	0.82	0.80	0.87	0.52	0.43	0.54	0.73				
V	0.85	0.28	0.74	0.51	0.62	0.73	0.74	0.79	0.82	0.71	0.79	0.36	0.41	0.60	0.82	0.91			
Y	0.80	0.20	0.70	0.49	0.70	0.75	0.62	0.67	0.67	0.67	0.81	0.37	0.52	0.43	0.77	0.83	0.85		
Zr	0.71	0.28	0.46	0.53	0.38	0.74	0.40	0.58	0.57	0.60	0.76	0.62	0.35	0.28	0.38	0.64	0.58	0.59	

Figure 58 Scatter plot matrix for geogenic inorganic elements



	Ba	Co	Cu	Hg	Ni	P	Pb	Ti	Zn
Ba									
Co	0.44								
Cu	0.54	0.62							
Hg	0.37	0.44	0.66						
Ni	0.44	0.82	0.61	0.44					
P	0.38	0.36	0.59	0.63	0.37				
Pb	0.50	0.42	0.73	0.77	0.32	0.60			
Ti	0.30	0.47	0.53	0.53	0.25	0.54	0.61		
Zn	0.50	0.43	0.67	0.43	0.37	0.44	0.63	0.43	



	Ca	Mg	Sr
Ca			
Mg	0.48		
Sr	0.94	0.44	

Figure 59 Scatter plot matrix for limestone alkaline earth metals

Figure 60 Scatter plot matrix for anthropogenic heavy metals

7.1.2 PAH compositions

PAH ratio plots may be used to further refine source attribution of PAH contamination (Section 4.3.2). For each city zone, PAH ratio plots have been produced to indicate possible sources of the observed concentrations. Figure 61 shows the scatter plot of ratios of BaA/(BaA+Chry) and Fl/(Fl+Pyr) for each sample point. Most points cluster in the upper right section of the plot in an area defined by BaA/(BaA+Chry)>0.35 and Fl/(Fl+Pyr)>0.5, attributing sources to grass/wood/coal combustion and general combustion respectively. Considering Dublin's history of domestic and industrial coal burning, the grass/wood/coal source can most likely be attributed to coal (Section 2.3.1).

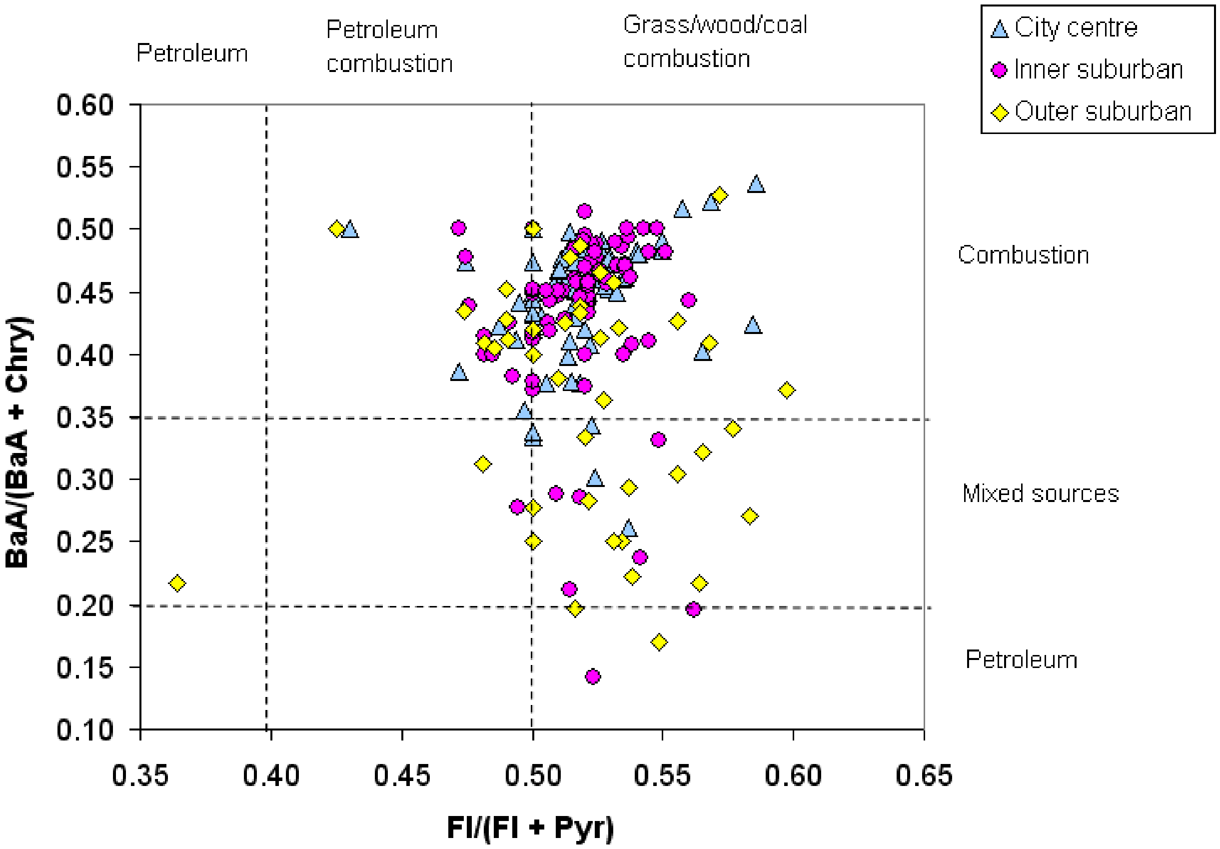
Many points straddle the Fl/(Fl+Pyr)=0.5 boundary between petroleum combustion and coal combustion. This is not unexpected in Dublin considering its heavy burden of traffic, especially in the city centre and along main arteries into and around the city. Although most points occur in the upper right "coal combustion" section, there is scatter in other sections indicating other multiple sources of PAH emission, such as traffic exhausts and petroleum products. Degradation of PAH compounds at different rates over time may also account for scatter in the plots. Creosote PAH ratios can be indistinguishable from combustion PAH ratios due to its formation during high temperature coal carbonisation (Yunker *et al.,* 2002). Contaminated imported fill may contain PAHs from a variety of sources and is difficult to characterise these clearly using PAH ratio plots.

Samples from the Inner City zone exhibit less scatter than the outer zones, possibly reflecting their proximity to historical PAH emission sources such as coal burning in industry and domestic homes. Coal burning emits heavier particulates than other types of combustion, meaning the coal PAH particulates are typically deposited close to the source of emission. Coal particulates are also associated with the sorption of high molecular weight PAHs, which makes them highly persistent in soils. More scattered source attribution in the outer zones could reflect long range deposition of particulates from various emission sources.

7.1.3 PCBs compositions

A graph showing the composition of individual PCB congeners detected in the greater Dublin area is shown in

Figure **62**. The graph indicates that the highly chlorinated PCB congeners 138, 153 and 180 are dominant in most samples where PCBs were detected. This composition would be consistent with Aroclor 1254 and 1260 mixtures found in European paints and electrical equipment. Low level detections for the less chlorinated PCBs indicate that there are not many recently active sources of PCBs at locations sampled, since less chlorinated PCBs such as congeners 28 and 52 degrade relatively rapidly from complex PCB mixtures compared to the other congeners. In other cities such as Glasgow, compositions of PCBs were relatively homogeneous in soils, indicating active and recent industrial contamination sources (Cachada *et al.*, 2009).



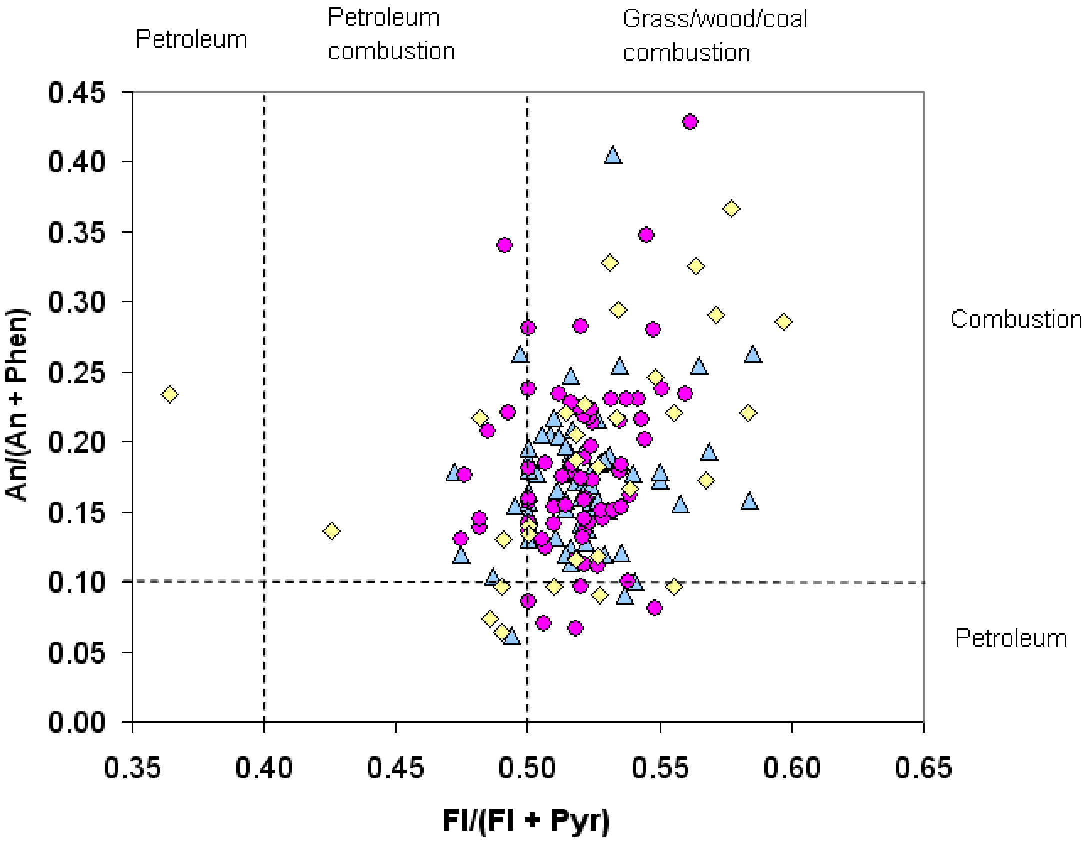


Figure 61 PAH ratio plots for city zones.

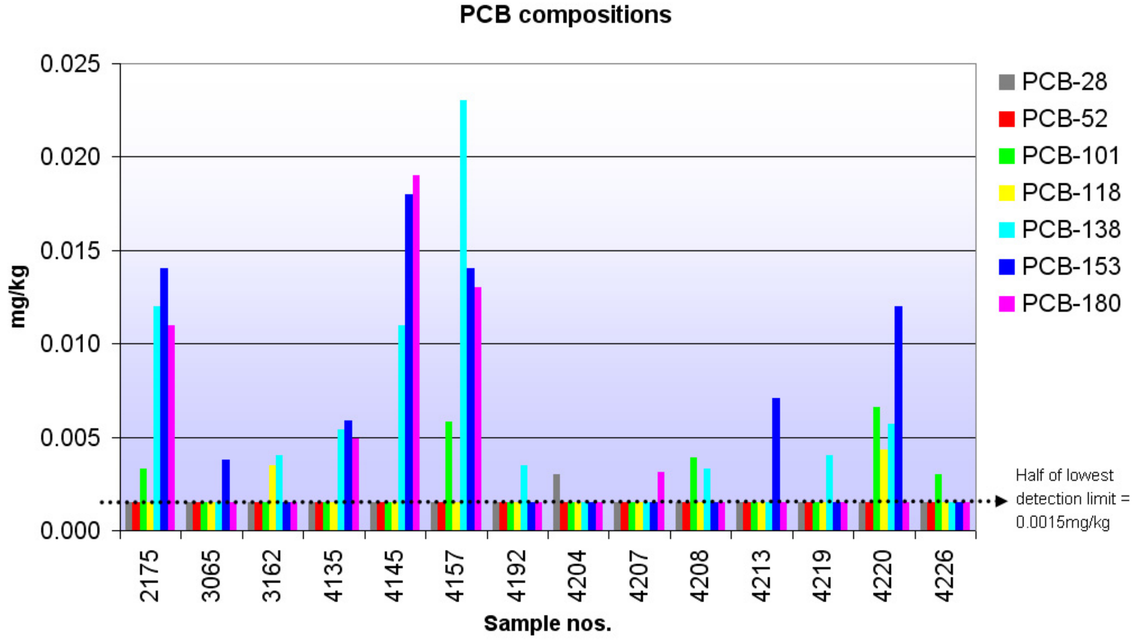


Figure 62 Compositions for PCBs detected in Dublin soils

7.2 Geochemical concentrations in made ground

As described in Section 2.1, much of Dublin's inner city topsoil is reclaimed or infilled land consisting of made ground, particularly in the docklands, port and low lowing coastal areas. Detailed work has not yet been carried out in Dublin which characterises made ground according to its provenance and constituent components. However, it is possible to compare the median concentrations of geochemical elements and compounds in made ground with those from natural ground in order to better understand the chemical makeup of made ground.

Table 11 shows the relative percentage difference between median inorganic element concentrations in topsoil in areas of made ground and areas of natural soil. For the anthropogenic metals Pb, Hg, Zn and Cu, median concentrations in made ground exceed those in natural ground by between 30% and 59%. In particular, made ground is enriched with Pb compared to natural ground, with a median level of 130 mg/kg in made ground compared to 70.9 mg/kg in natural ground.

Other inorganic elements (Sr, Mg, P, Ti, Ba and Na) show some influence of anthropogenic activities with enrichments in made ground exceeding those in natural soil by between 10% and 33%. Activities which are likely to have contributed to enhanced heavy metals in made ground include diffuse atmospheric deposition of particulates from coal burning and traffic; and the use of contaminated fill materials, such as fly ash, coal clinker, construction rubble and domestic waste to fill and landscape low-lying land.

The mainly geogenic elements of Zr, Al, La, Ce, B, Y, K, Sc and Mn are notably depleted in inner city made ground, with levels between 10% and 14% lower than those in natural ground. This depletion of naturally occurring elements reflects the composition of made ground, which may have a low content of geological materials of local origin.

Sixty-three topsoil samples taken on made ground were tested for PAHs. In Figure 63 a boxplot is shown for ΣPAH_{16} concentrations in natural soil and made ground. The median level of ΣPAH_{16} in made ground was 5.74 mg/kg, which exceeds the median level in natural ground (2.59 mg/kg) by 75%.

These data indicate that made ground has significantly more geochemical contaminants than natural soil in the greater Dublin area. This is likely to be due to a combination of anthropogenic contaminants in made ground and the increased burden of atmospheric deposition which occurs on made ground due to its occurrence largely in the inner city.

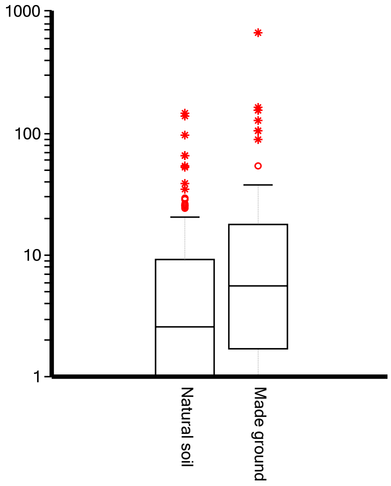


Figure 63 Boxplot comparing median concentrations of ΣPAH_{16} in natural soil and made ground.

	Median, mg/kg		
	Natural soil	Made ground	RPD
Pb	70.9	130	59%
Hg	0.20	0.29	35%
Sr	120	168	33%
Zn	168	235	33%
Cu	34.3	46.4	30%
Mg	4,225	4,685	10%
Ti	199	220	10%
P	1,040	1,145	10%
Ba	174	192	10%
Na	655	687	5%
Co	9.56	9.89	3%
As	13.4	13.7	2%
Ca	35,400	36,000	2%
Be	1.36	1.34	-1%
Si	571	563	-1%
Fe	22,150	21,800	-2%
Ni	41.1	39.9	-3%
Cd	1.75	1.66	-6%
Li	28.5	27.0	-6%
Cr	44.4	41.6	-7%
V	72.5	66.8	-8%
Zr	13	11.8	-10%
Al	29,150	26,400	-10%
La	18	16.3	-10%
Ce	32.3	29	-11%
B	34	30.5	-11%
Y	15.2	13.6	-11%
K	7,480	6,650	-12%
Sc	6.2	5.51	-12%
Mn	960	836	-14%

Table 11 Relative percentage difference between median inorganic element concentrations in natural and made ground.

7.3 Comparison with other cities

Results between different studies should not be compared like-for-like unless the environmental medium (topsoil, subsoil, etc), sampling method, sample preparation, analytical methods and detection limits are comparable (Johnson & Ander, 2008). As such it is not possible to directly compare results from the Dublin SURGE Project with urban geochemical surveys carried out in other cities. However, it is informative to review results from other cities in order to put the Dublin results into a broad context.

7.3.1 Inorganic elements

The British Geological Survey as part of the G-Base and Tellus programmes mapped inorganic elements in topsoil in 26 UK cities. Soil concentrations were interpreted in terms of the geological setting and industrial history of each city. Table 12 shows median concentrations for eight anthropogenic heavy metals in three UK cities with varying industrial histories. Data from Dublin is included for reference. Belfast's historical industry, like Dublin, was focussed on port activities but it also had significant heavy engineering operations relating to shipbuilding in the 19th century (Nice, 2010). The Belfast survey reported natural Cr and Ni anomalies in topsoil in the northwest of the Belfast metropolitan area, associated with the Antrim Basalts (Nice, 2010).

Industrial activities in 19th and 20th century Swansea were based on coal mining, port operations and metal smelting and processing (Morley and Ferguson, 2001). These activities are likely to have had a strong influence on regional geochemistry in Swansea, which is characterised by elevated levels of heavy metals. Lincoln is a pre-Roman city with low to moderate levels of heavy metals, reflecting an industrial history based on light industry and manufacturing (O'Donnell, 2005).

A qualitative comparison of Dublin with these UK cities indicates that Dublin has moderate concentrations of heavy metals, reflecting a diverse industrial past focussed on port operations and small-scale local industry rather than large-scale heavy industry.

	mg/kg							
	As	**Cd**	**Co**	**Cu**	**Ni**	**Pb**	**V**	**Zn**
Dublin	*13.4*	*1.74*	*9.58*	*35.0*	*41.0*	*73.7*	*72.1*	*172*
Belfast	10.1	0.3	20.3	52.8	65.9	67.7	113	118
Swansea	53	2	23	116	37	225	85	316
Lincoln	11	0.45	12	17	14	55	54	61

Table 12 Median concentrations for anthropogenic heavy metals in UK cities (data compiled from Nice (2010), O'Donnell (2005) and Morley and Ferguson (2001)).

7.3.2 POPs

As part of the URBSOIL Project, (Morillo *et al.*, 2007, and Cachada *et al.,* 2009) mapping of POPs in topsoil was undertaken in Glasgow, UK; Torino, Italy; and Ljubljana, Slovenia (PAHs and PCBs); and Uppsala, Sweden and Aveiro, Portugal (PCBs). Results for Σ15 PAHs and Σ7 PCBs in these cities are given in Table 13 and Table 14 for reference. Glasgow has a history of heavy industry and this is reflected in the elevated medians of 8.34 mg/kg for Σ15 PAHs and 0.022 mg/kg for Σ19 PCBs.

PAH and PCBs were measured in Belfast as part of the Tellus Project. The survey maxima in Belfast were 75.2 mg/kg for Σ16 PAHs and 0.132 mg/kg for Σ7 PCBs (M.Young, pers. comms., 2010)[1]. The maxima for Σ16 PAHs and Σ7 PCBs in Dublin were 661 mg/kg and 0.0603 mg/kg respectively. Although it is difficult to compare these results qualitatively it is likely that Dublin's soil is more impacted than Belfast's on a city-wide basis due to its much larger population.

The median PAH level measured in Dublin (3.47 mg/kg) appears to be in between median levels measured for a heavily industrialised city like Glasgow and less industrialised European cities. The maximum ΣPCB_7 concentration measured in Dublin as part of the SURGE project (0.0603 mg/kg) appears to be broadly consistent with or lower than those found in other European cities.

City	PAHs	Median, mg/kg
Dublin	*Σ16*	*3.47*
Glasgow, UK	Σ15	8.34
Torino, Italy	Σ15	0.70
Ljubljana, Slovenia	Σ15	0.79

Table 13 Median concentrations of PAHs measured in three European cities (Morillo *et al.*, 2007)

	Σ19 PCBs, mg/kg	
	Median	Max
Dublin (Σ7 PCBs)	-	*0.0603*
Aveiro, Portugal	0.0079	0.073
Glasgow, Scotland	0.0220	0.078
Ljubljana, Slovenia	0.0068	0.048
Torino, Italy	0.0140	0.172
Uppsala, Sweden	0.0057	0.077

Table 14 Data for Σ19 PCBs measured in five European cities (Cachada *et al.,* 2009).

7.4 Bull Island and harbour sediments

Bull Island is a sand island in Dublin Bay which began to accumulate almost 200 years ago in response to the building of the North Bull Wall in 1824. As such it represents a young geological deposit which has been subject to the effects of human activities only in relatively recent times. An examination of results from four soil samples taken on Bull Island indicate that most inorganic elements are relatively depleted at Bull Island. This is not unexpected as sand has a low attenuation capacity for pollutants due to its low organic matter content. However, concentrations above the respective survey median level occur on the island for Pb, Hg and As. This supports the interpretation of Pb, Hg and As concentrations as being partly derived from post-industrialisation atmospheric deposition due to human activities.

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[1] Due to high high proportions of censored data (data <MDL) it was not possible to report median levels for Belfast PAHs and PCBs results.

However, there also may be minor direct inputs of these elements from historical activity at Bull Island such as landfilling and military activity.

Work carried out by the British Geological Survey has demonstrated that harbour sediments in estuaries of industrial cities bear the chemical signature of historical industrial activities. Depth profiles of harbour sediments in the Mersey estuary, UK (Vane *et al.,* 2007) and the Clyde estuary, UK (Vane *et al.,* 2011) show the rise, peak and decline of PCB use, the rise of pyrogenic and petrogenic PAH sources and the decline of coal-related PAH inputs. Lead isotope analysis in the Clyde estuary sediments indicated various proportions of background Pb, British ore/coal Pb, leaded petrol and industrial Pb in harbour sediments (Vane *et al.,* 2011). Harbour and estuary sediments can become contaminated through runoff from contaminated soil, industrial discharges to the harbour, atmospheric deposition of combustion particles and fuel and cargo leaks from ships. Harbour sediment contamination can impact water quality, aquatic organisms and contaminant levels in fish and shellfish. It is recommended that a study of the Liffey estuary and Dublin Bay is completed to assess the contaminant levels in aquatic sediments.

8 Conclusions

8.1 Heavy metals

Results for heavy metals indicate that the concentrations of Pb, Cu, Zn and Hg are strongly influenced by human activities. The concentrations of these metals are elevated in the docklands and in inner city and heavy industry areas. Sources of heavy metals in these areas include historic industry such as metal and chemical works, coal burning in homes and industry, reuse of contaminated soil and modern traffic.

Lead concentrations are higher in inner city locations than outer city areas, a trend which can be attributed to the use of leaded paint and petrol in addition to the sources described above.

Concentrations of other inorganic elements in topsoil in the greater Dublin area show patterns which are strongly related to regional bedrock parent material (limestones in the Dublin basin region and the Leinster granites in southern Co. Dublin).

8.2 PAHs

PAHs are amongst the most common POPs present in the environment today and this is reflected in the Dublin SURGE Project results. PAHs were detected across the greater Dublin area, with highest concentrations in the City Centre zone declining with distance from the historic inner city to the outer suburbs. This trend was not unexpected, considering that PAH concentrations are generally higher in urban areas due to the intensity of human activities over a long period of time.

The compositions of PAH compounds measured in the soil samples were consistent with a long history of coal burning in domestic fires and industrial processes which caused diffuse atmospheric pollution and deposition of PAHs in soils. Domestic coal burning produces more PAH emissions than industrial coal burning and a significant air pollution problem from coal smoke resulted from widespread domestic coal burning in Dublin in the 1980s. Since the ban on the sale, marketing and distribution of bituminous coal in Dublin in 1990 there has been a dramatic improvement in air quality in Dublin.

Traffic emissions are now also improving due to increased vehicle engine efficiency. It is likely that PAH concentrations in Dublin soils due to atmospheric deposition of traffic and coal combustion emissions will gradually decline over time, resulting in some improvement in soil quality.

Historical landfilling and land reclamation may have left a significant legacy of PAH pollution in many older city areas. There is anecdotal evidence of the historical use of industrial residues such as coal clinker to fill low lying land around the city centre, and more modern use of waste as a fill material. It is possible that a number of modern sources are acting as point sources of PAH contamination in the environment, such as creosote treated wood products. Bonfire burning was observed in several residential open spaces during the soil sampling campaign around Halloween and the potential of bonfires to emit organic compounds to the air and to the soil is noted.

The popularity of allotments is increasing. Land that is being considered for allotment use should be tested for soil contaminants as a priority over testing for soil agricultural properties. Appropriate investigations should be undertaken to ensure that such land is fit for purpose with regard to the protection of human health from soil contaminants.

8.3 PCBs

Results for PCBs in soil indicate isolated, low level detections of PCBs in Dublin, mainly in the city centre, which are broadly consistent with levels detected in other European cities which were not heavily industrialised.

Detections consisted mainly of highly chlorinated PCB congeners which indicate that contamination is probably associated with historical industrial sources and old paint rather than modern, active sources.

8.4 Overall trends

The overall trends observed in geochemical concentrations are as follows:

- A strong concentric pattern of higher concentrations of PAHs and anthropogenic heavy metals in the inner city, declining with distance from the inner city.
- Higher median concentrations of PAHs and anthropogenic heavy metals, particularly Pb, in made ground than in natural ground.

9 Recommendations and further work

Dublin's inner city has a history of over 1,000 years of human habitation and was industrialised in the mid-19th century. As such, the elevated concentrations of PAHs and anthropogenic metals, especially Pb, in the inner city area observed in this survey are not unexpected. Advances in environmental protection have been made in recent decades in Dublin with the bituminous coal burning ban, the regulation and licensing of industry and remediation of many inner city contaminated sites through redevelopment. Although traffic volumes have increased over the years and vehicle emissions are now the main pressure on Dublin's air quality, vehicle engines are becoming cleaner. These factors are reducing heavy metal and PAHs emissions which can impact on topsoil quality. However active measures are required to ensure good land management practices in relation to the reuse of contaminated soil and dealing with contaminated soils in playgrounds and parks.

9.1.1 Publicly accessible lands

, It should be ensured that publicly accessible lands, such as parks, playing fields, playgrounds and allotments are free of contaminant sources which can cause PAH and heavy metal, especially Pb, contamination.

- Although the use of creosote treated wood products and certain recycled tyre products are restricted by law, they may remain in some public recreational areas. Management practices for public recreational areas should take this possibility into account.

- Management practices for public lands should take into account the potential existence of contaminated fill materials that may have been used in the past and take measures to ensure that they do not pose a risk to the health of users of such areas. Modern landscaping activities should ensure that topsoil or fill materials are sourced from reputable suppliers and are determined as fit for purpose through laboratory testing for organic and metal contaminants.]

- Continued efforts by local authorities to discourage bonfires in parks and to implement bonfire cleanup strategies are recommended.

- The demand for allotments in Dublin is increasing, and the importance of assessing soil contamination on land designated for allotment use must be emphasised, especially where the land had been associated with previous on-site or nearby industrial activity or waste dumping. Appropriate site investigations should be undertaken to ensure that such land is fit for purpose with regard to the protection of human health from soil contaminants. Testing soil for contaminants including heavy metals, PAHs and PCBs should take priority over soil tests for agricultural properties during allotment designation.

9.1.2 Contaminated land guidance for Ireland

It is recommended that a contaminated land guidance and regulatory regime is put in place for Ireland, in order to prevent deterioration of

Ireland's soil resource, especially in urban areas. Experience from the UK, the Netherlands and Norway shows that establishment of authoritative contaminated land guidance relies on the close cooperation of health authorities, regulators and environmental experts and it is recommended that an inter-agency group of such experts be established in Ireland.

9.1.3 Further work

- The survey did not target areas of suspected PCB contamination and a survey targeting sites in direct proximity to painted surfaces such as old metal structures (e.g. railings, bridges, goal posts) and building exteriors would give a better understanding of sources of PCBs in the modern urban environment.
- More research is needed on the effects of creosote treated wood products, recycled tyre products and cigarette waste on the soil environment and human health, especially in playgrounds and parks.
- As organic pollutants such as PAHs and PCBs persist in soil for many years, it is recommended that repeat baseline surveys be carried out at regular intervals in the future, to monitor overall soil quality in response to anticipated reductions in atmospheric pollution and improved land management practices.
- Studies in the UK have demonstrated that harbour sediments in industrialised cities are impacted by heavy metal and POP pollution. It is recommended that a study is completed to assess the contaminant levels in aquatic sediments in the Liffey estuary and Dublin Bay.
- Results of the Dublin SURGE Project could be used to aid epidemiological studies by correlating soil contaminant concentrations with health outcome data such as cancer incidence.
- Site-specific assessment of heavy metals should take into account speciated metal compound concentrations, bioavailability of these substances and site histories, especially if there is doubt over the provenance of metal concentrations in soils (natural or anthropogenic). Particular attention should be paid to Pb and As in topsoil in Dublin, where there may be no clear distinction between anthropogenic and natural concentrations from total element determination tests alone.
- Detailed work has not yet been carried out in Dublin which characterises made ground according to its provenance and constituent components. Such work could contribute to more effective management of contamination issues associated with made ground in public areas.

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UK DoE (1995e) *Industry Profile. Metal manufacturing, refining and finishing works. Iron and steelworks.* UK Department of the Environment.

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Appendix A – Analytical QA/QC

Figure A1 Field duplicate scatter plots

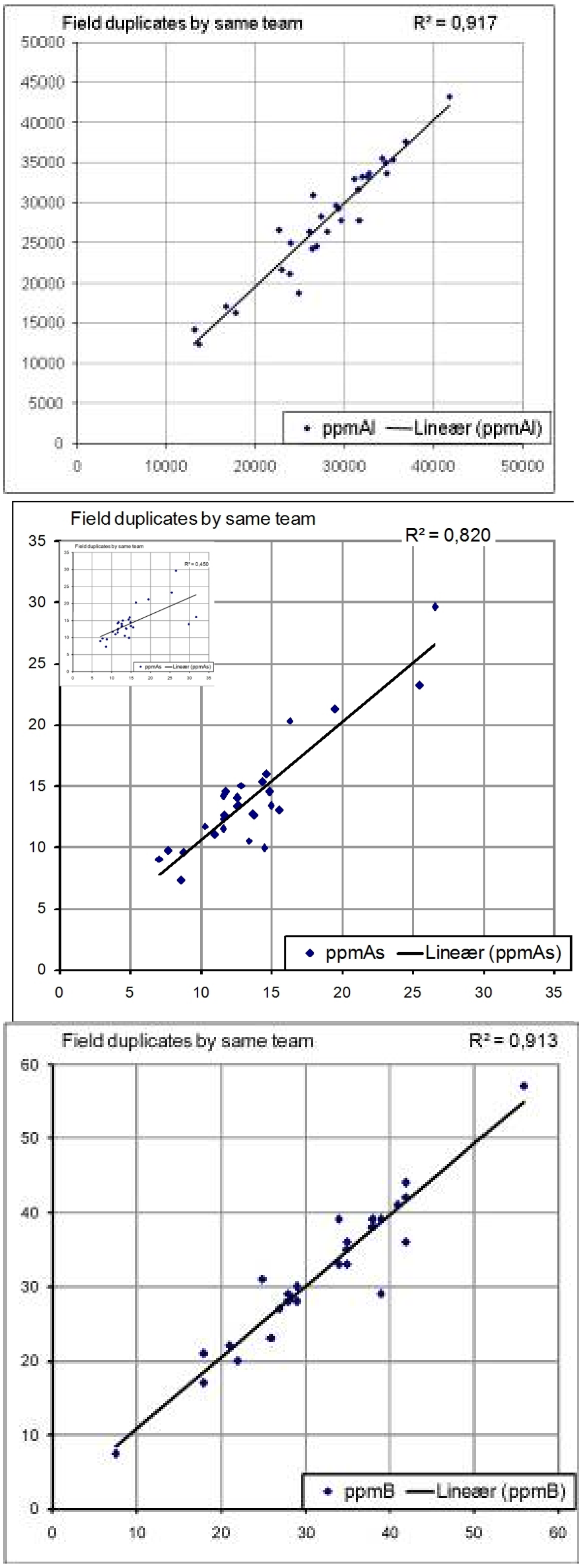
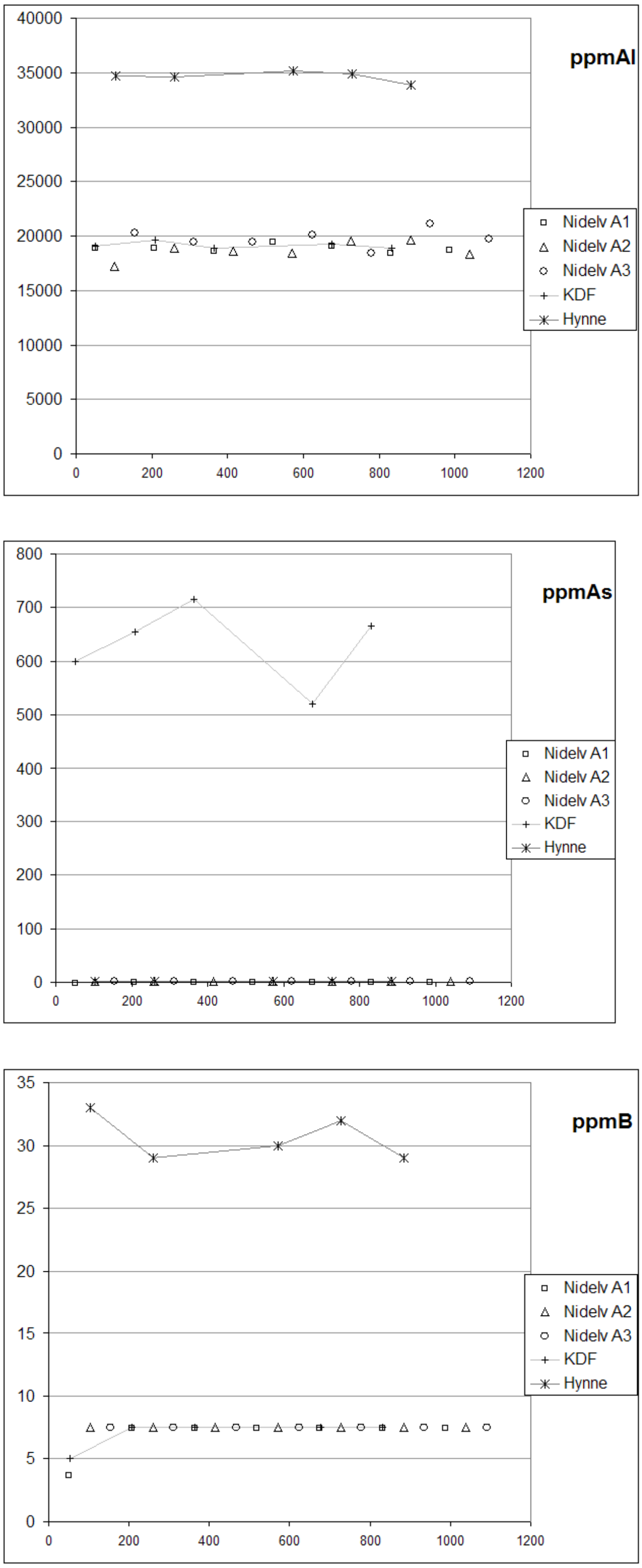
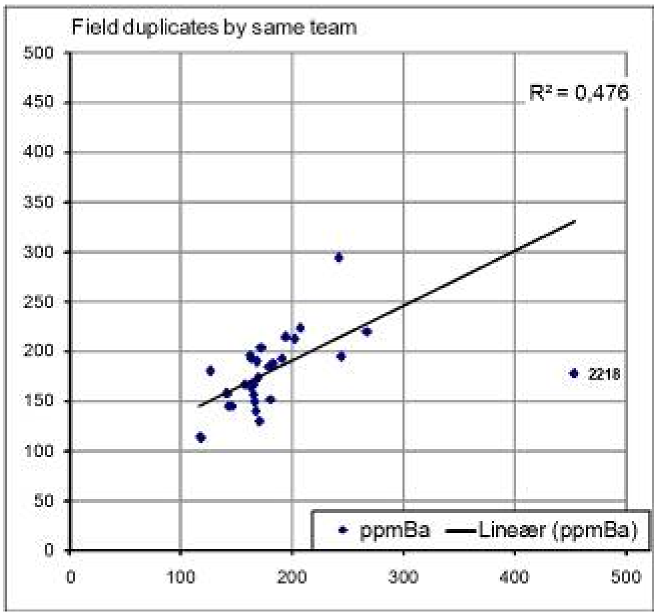
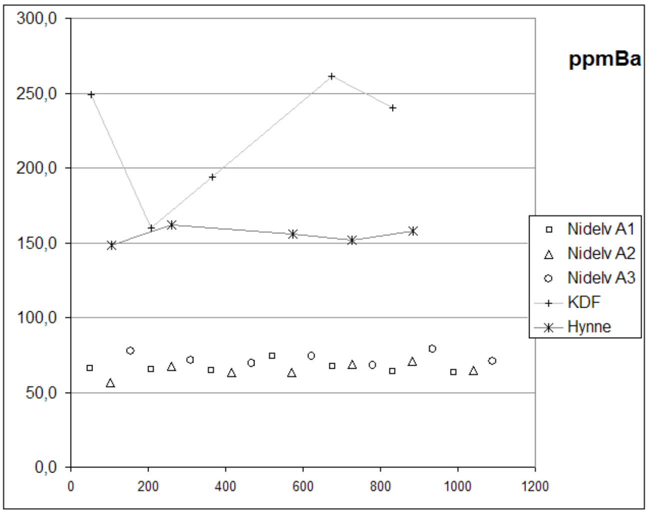
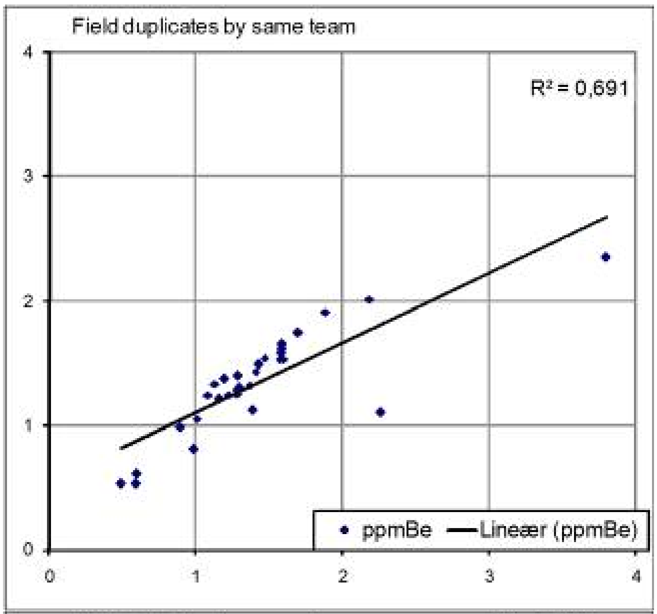


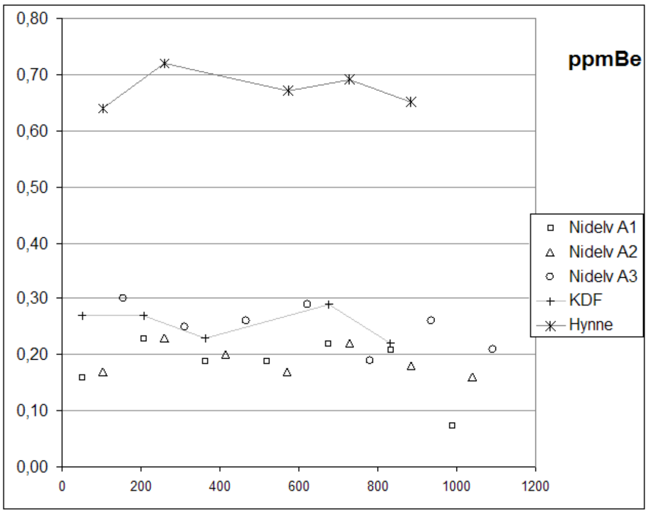
Figure A2 Element concentrations versus sequence no.

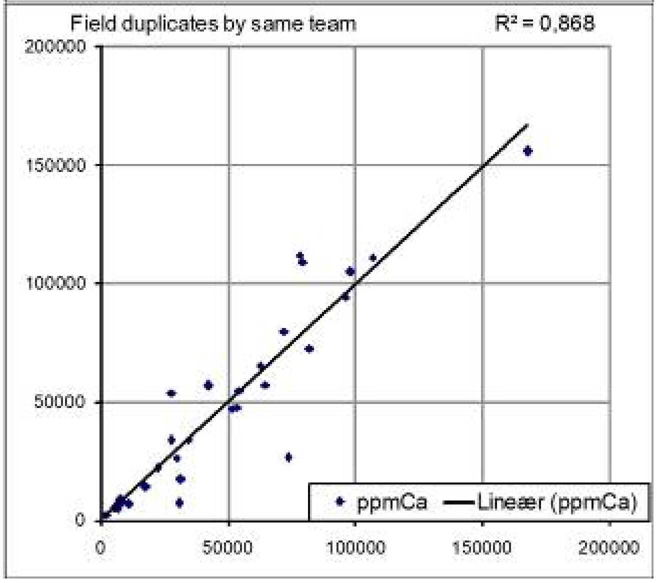


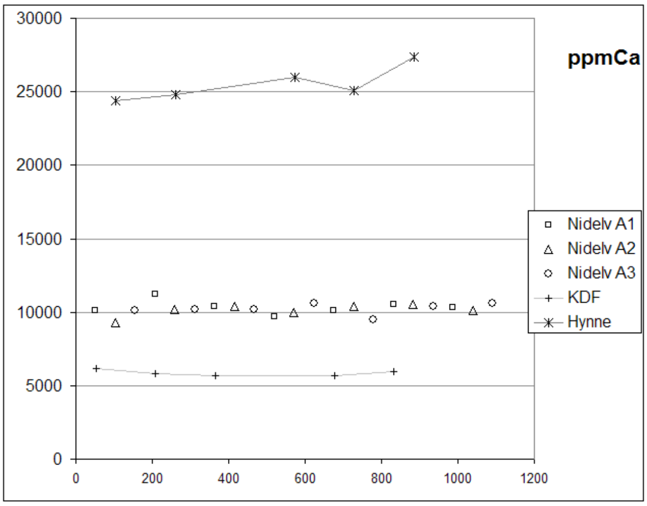

Field duplicates by same team
R² = 0,476
2218
ppmBa
Lineær (ppmBa)
0
50
100
150
200
250
300
350
400
450
500
0
100
200
300
400
500

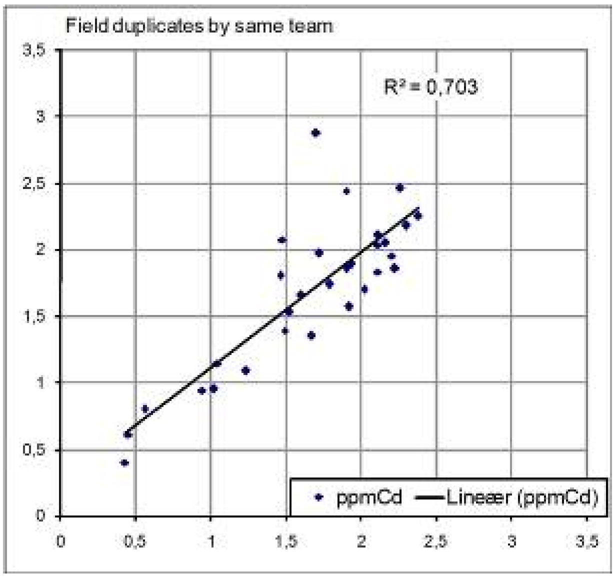

ppmBa
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne
0,0
50,0
100,0
150,0
200,0
250,0
300,0
0
200
400
600
800
1000
1200

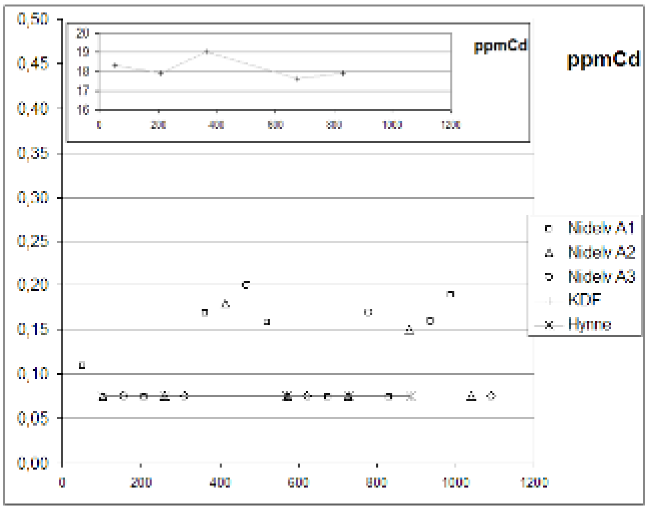

Field duplicates by same team
R² = 0,691
ppmBe
Lineær (ppmBe)
0
1
2
3
4
0
1
2
3
4

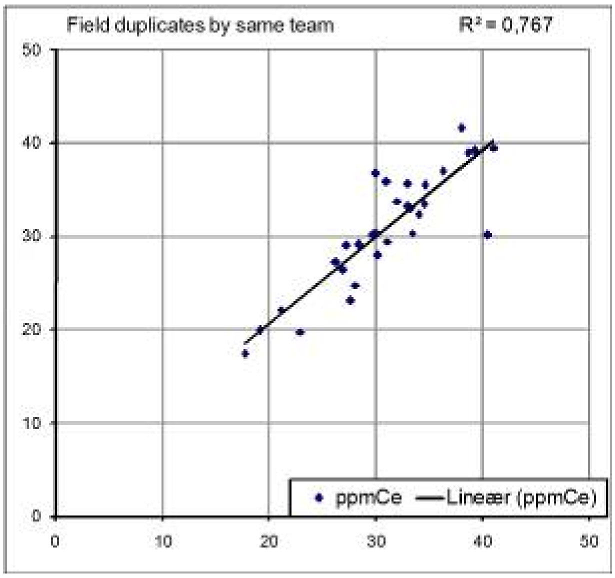

ppmBe
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne
0,00
0,10
0,20
0,30
0,40
0,50
0,60
0,70
0,80
0
200
400
600
800
1000
1200

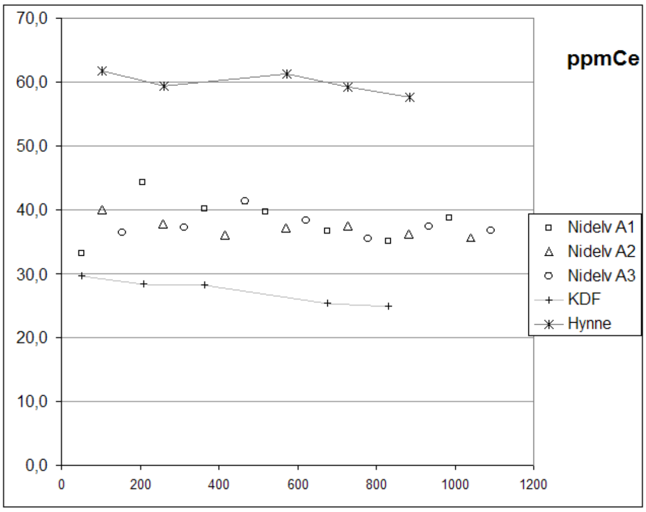

Field duplicates by same team
R² = 0,868
ppmCa
Lineær (ppmCa)
0
50000
100000
150000
200000
0
50000
100000
150000
200000

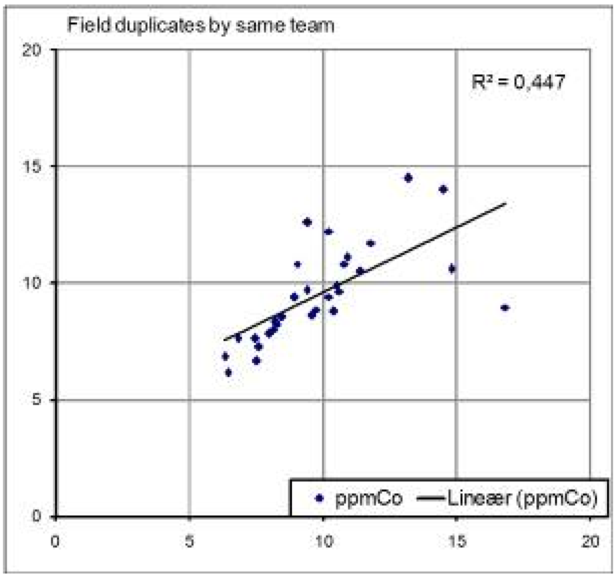

ppmCa
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne
0
5000
10000
15000
20000
25000
30000
0
200
400
600
800
1000
1200

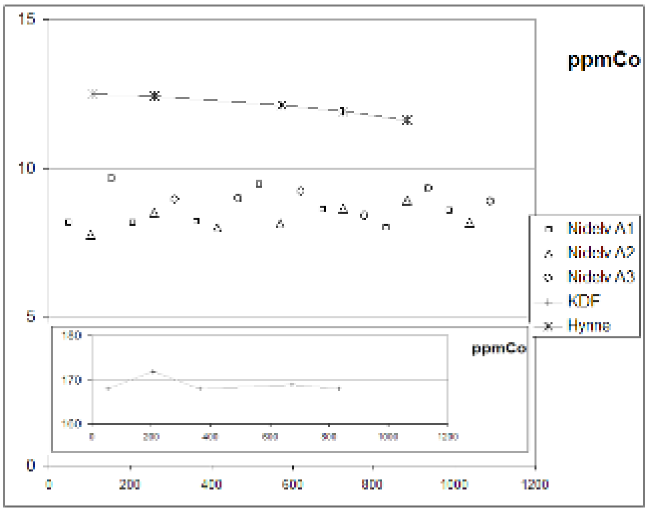

Field duplicates by same team
R² = 0,703
3,5
3
2,5
2
1,5
1
0,5
0
0
0,5
1
1,5
2
2,5
3
3,5
ppmCd
Lineær (ppmCd)

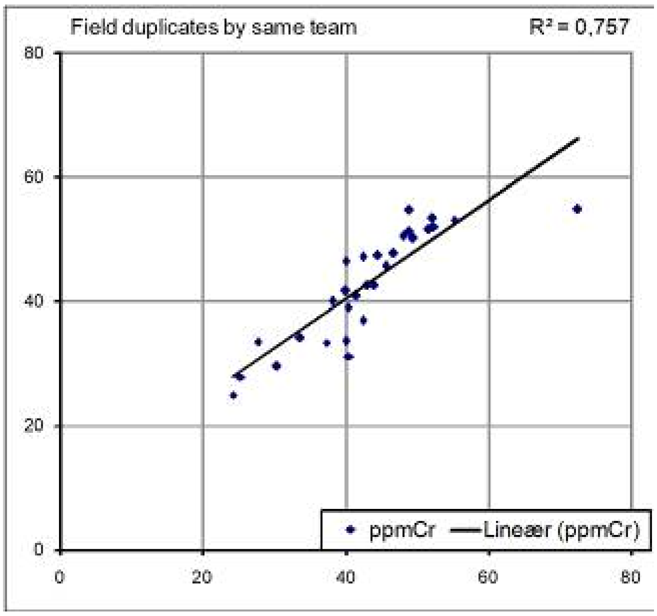

0,50
0,45
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
0,00
0
200
400
600
800
1000
1200
20
19
18
17
16
ppmCd
ppmCd
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

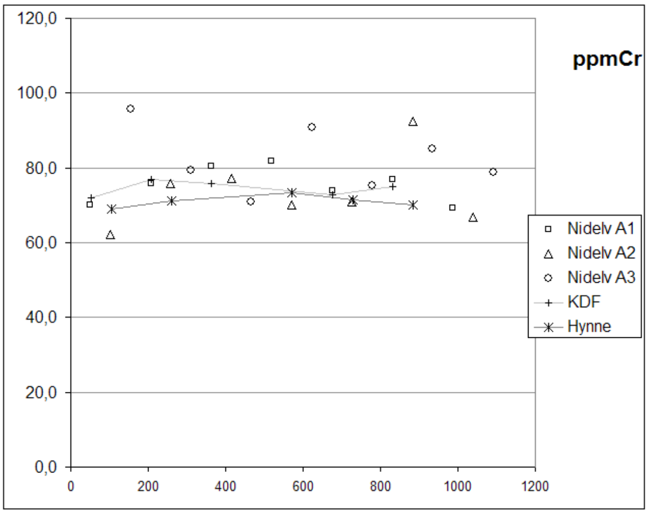

Field duplicates by same team
R² = 0,767
50
40
30
20
10
0
0
10
20
30
40
50
ppmCe
Lineær (ppmCe)

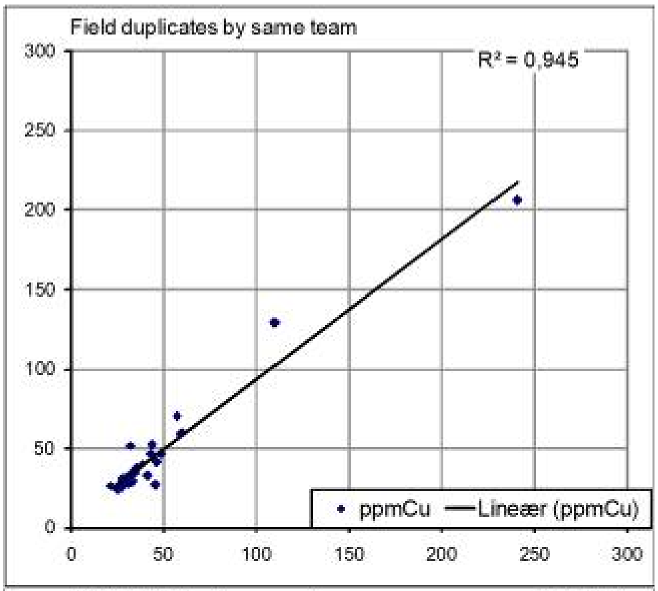

70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
0
200
400
600
800
1000
1200
ppmCe
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

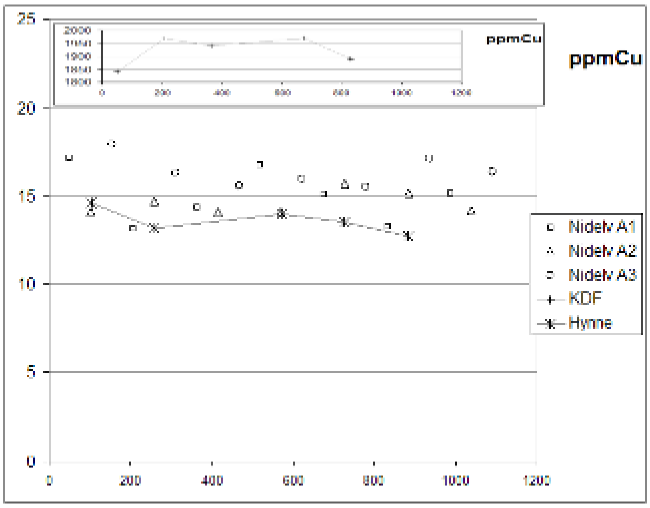

Field duplicates by same team
R² = 0,447
20
15
10
5
0
0
5
10
15
20
ppmCo
Lineær (ppmCo)

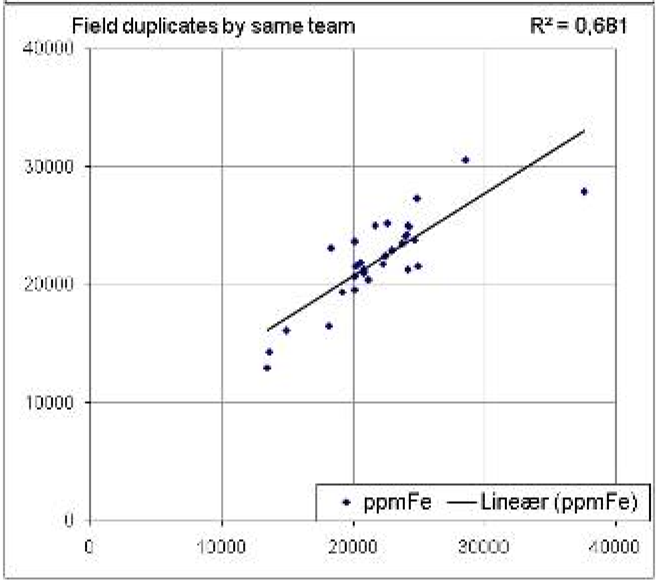

15
10
5
0
0
200
400
600
800
1000
1200
ppmCo
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne
180
170
160
ppmCo

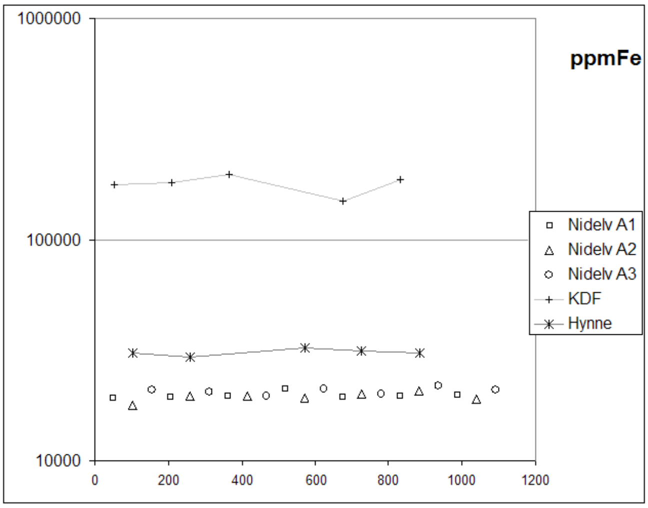

Field duplicates by same team
R² = 0,757
80
60
40
20
0
0
20
40
60
80
ppmCr
Lineær (ppmCr)

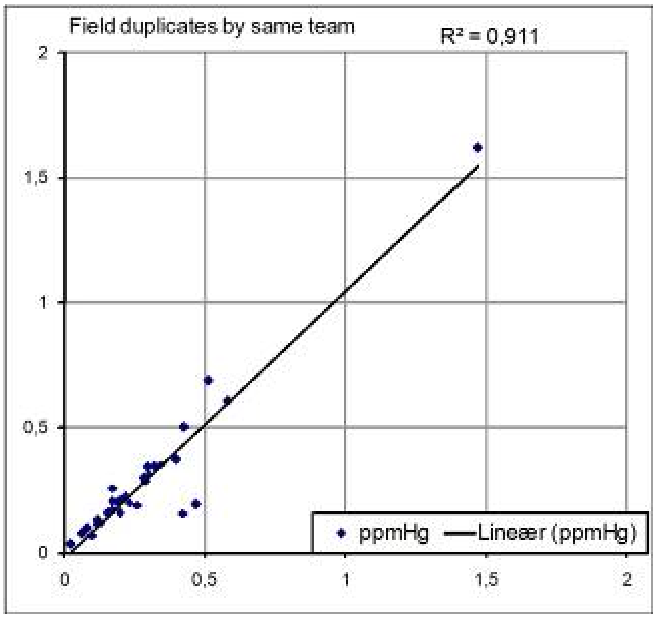

ppmCr
120,0
100,0
80,0
60,0
40,0
20,0
0,0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

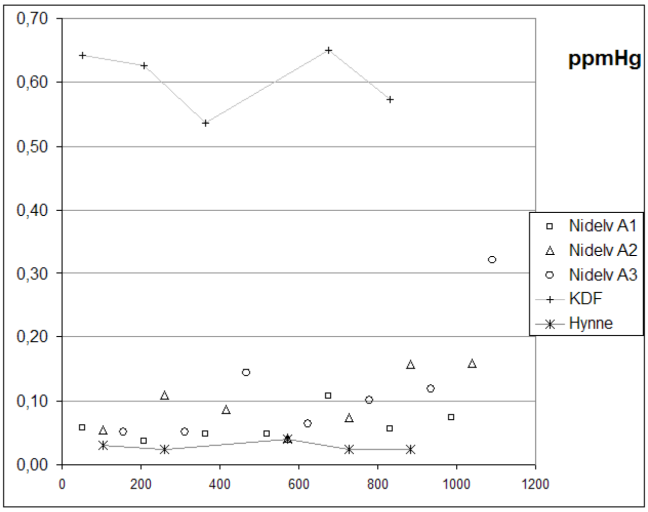

Field duplicates by same team
R² = 0,945
300
250
200
150
100
50
0
0
50
100
150
200
250
300
ppmCu
Lineær (ppmCu)

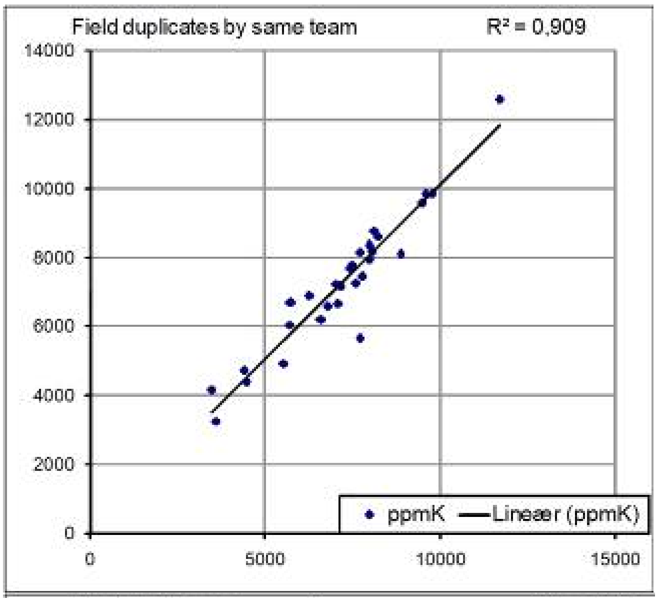

ppmCu
25
20
15
10
5
0
0
200
400
600
800
1000
1200
ppmCu
2000
1900
1800
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

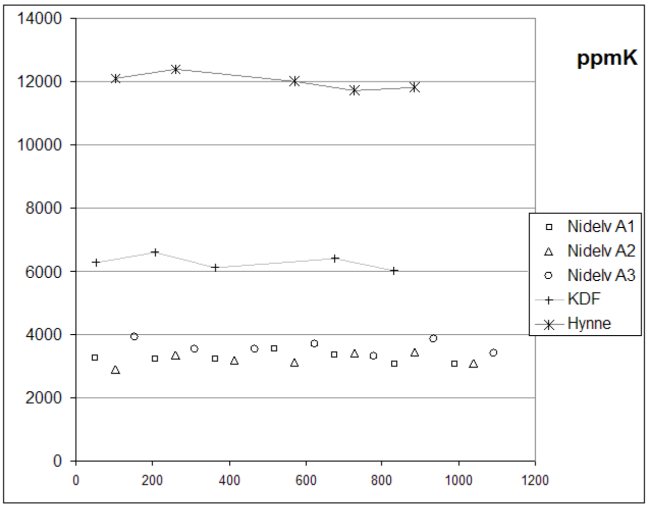

Field duplicates by same team
R² = 0,681
40000
30000
20000
10000
0
0
10000
20000
30000
40000
ppmFe
Lineær (ppmFe)

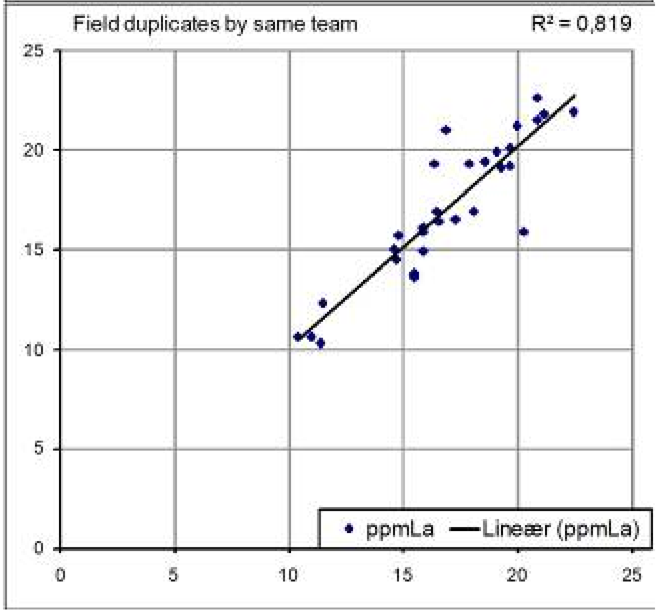

ppmFe
1000000
100000
10000
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

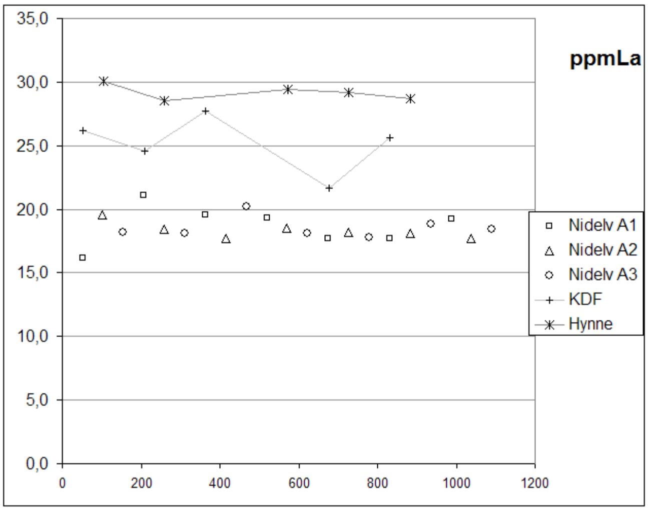

Field duplicates by same team
R² = 0,911
2
1,5
1
0,5
0
0
0,5
1
1,5
2
ppmHg
Lineær (ppmHg)

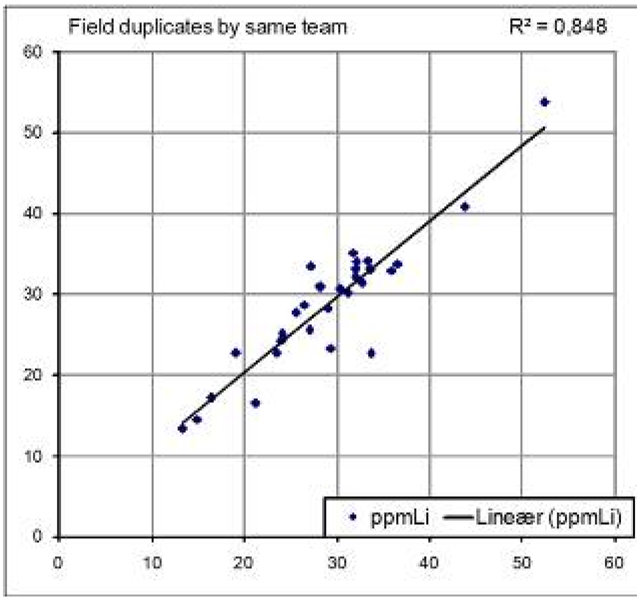

ppmHg
0,70
0,60
0,50
0,40
0,30
0,20
0,10
0,00
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

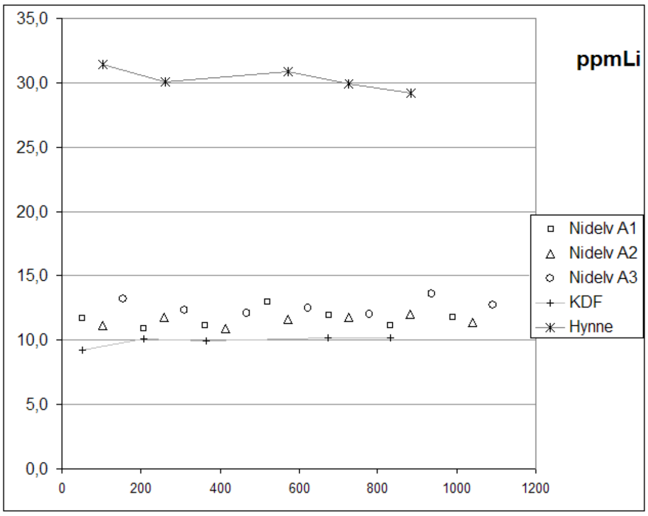

Field duplicates by same team
R² = 0,909
14000
12000
10000
8000
6000
4000
2000
0
0
5000
10000
15000
ppmK
Lineær (ppmK)

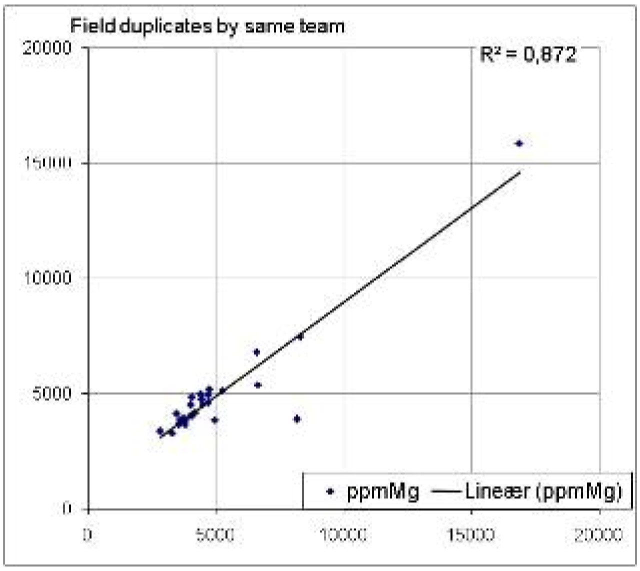

ppmK
14000
12000
10000
8000
6000
4000
2000
0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

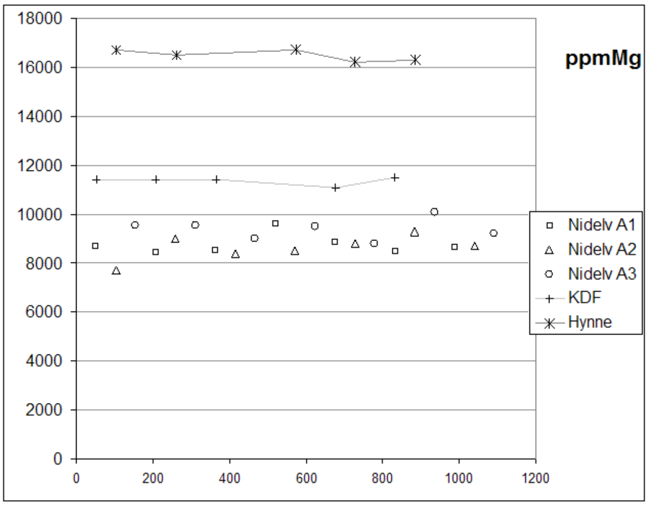

Field duplicates by same team
R² = 0,819
25
20
15
10
5
0
0
5
10
15
20
25
ppmLa
Lineær (ppmLa)

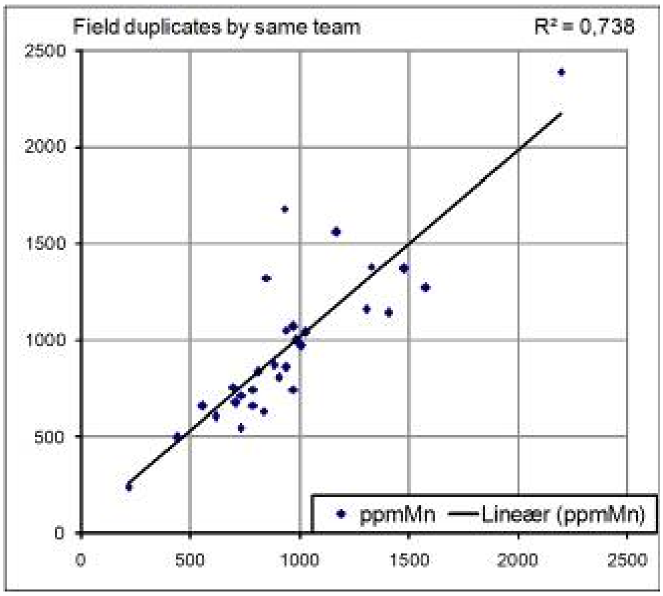

ppmLa
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

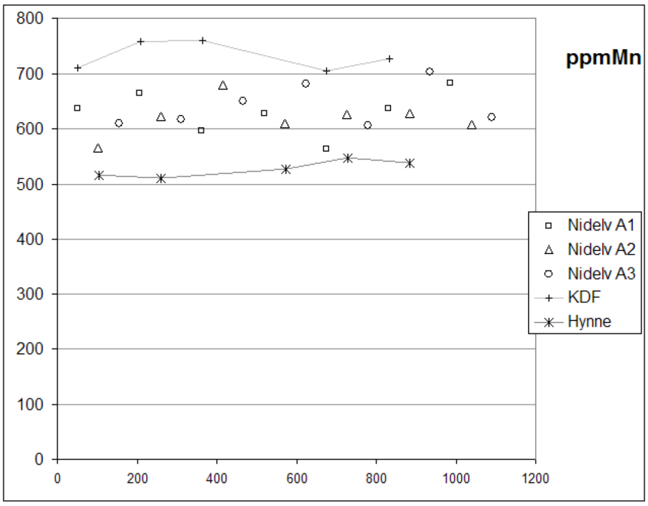

Field duplicates by same team
R² = 0,848
0
10
20
30
40
50
60
ppmLi
Lineær (ppmLi)

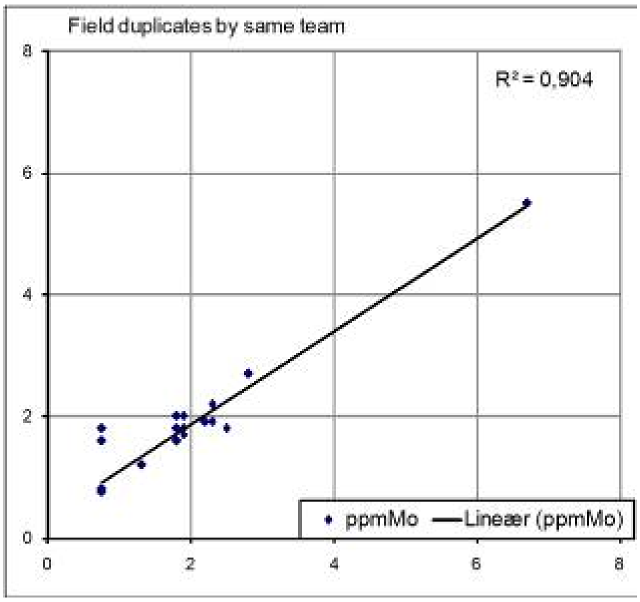

ppmLi
0,0
5,0
10,0
15,0
20,0
25,0
30,0
35,0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

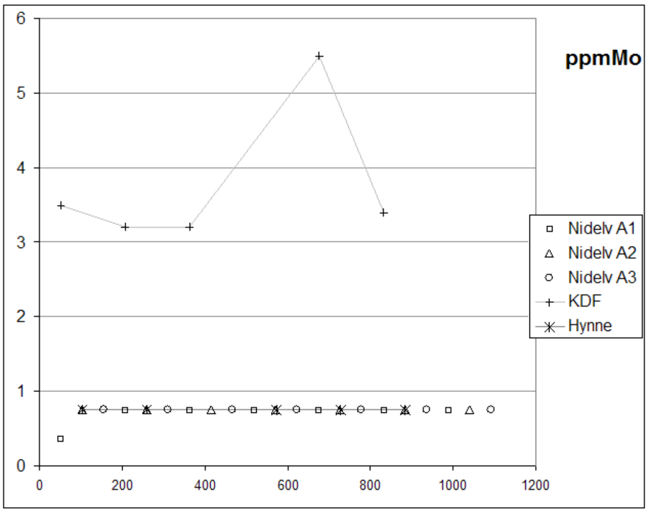

Field duplicates by same team
R² = 0,872
0
5000
10000
15000
20000
ppmMg
Lineær (ppmMg)

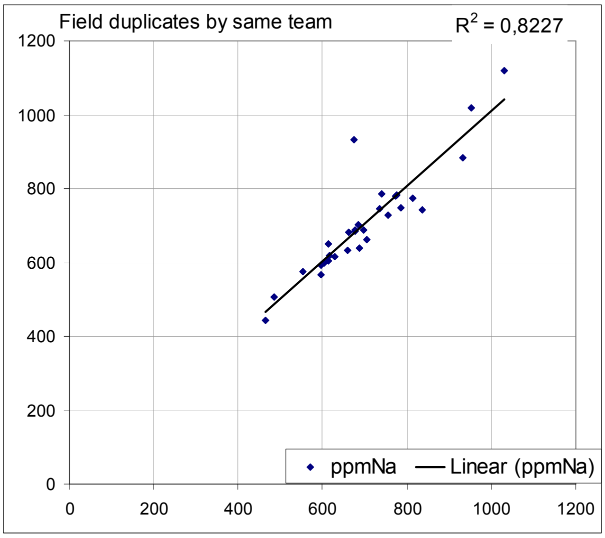

ppmMg
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

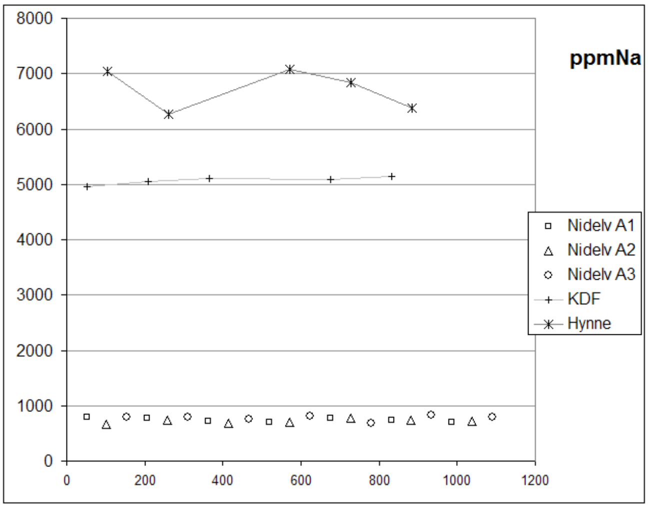

Field duplicates by same team
R² = 0,738
0
500
1000
1500
2000
2500
ppmMn
Lineær (ppmMn)

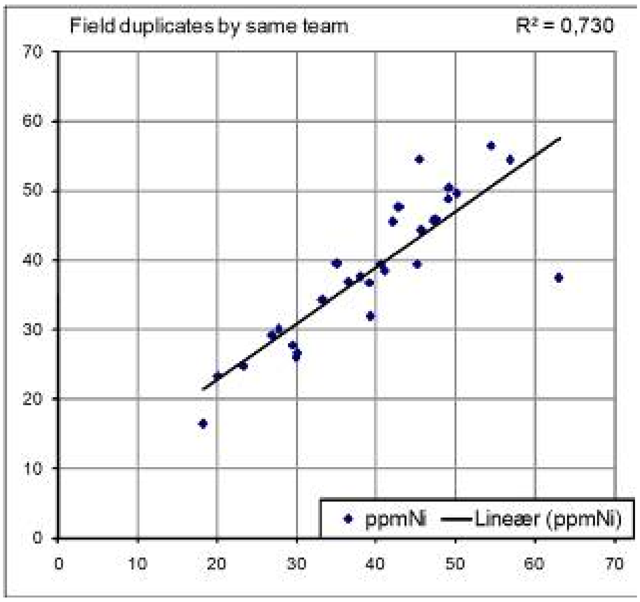

ppmMn
0
100
200
300
400
500
600
700
800
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

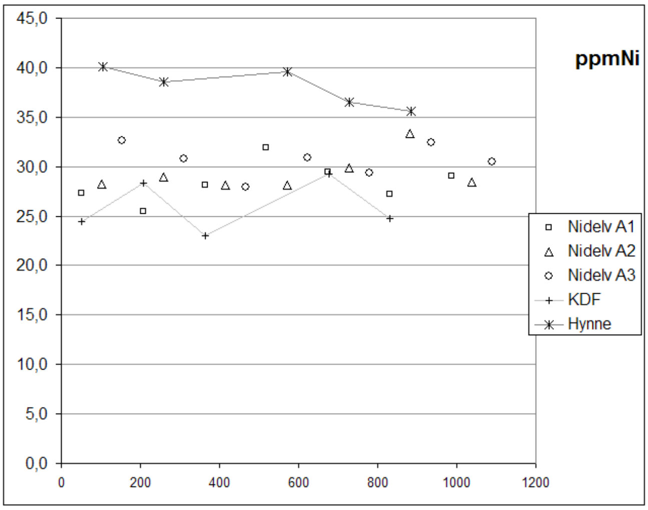

Field duplicates by same team
R² = 0,904
8
6
4
2
0
0
2
4
6
8
ppmMo
Lineær (ppmMo)

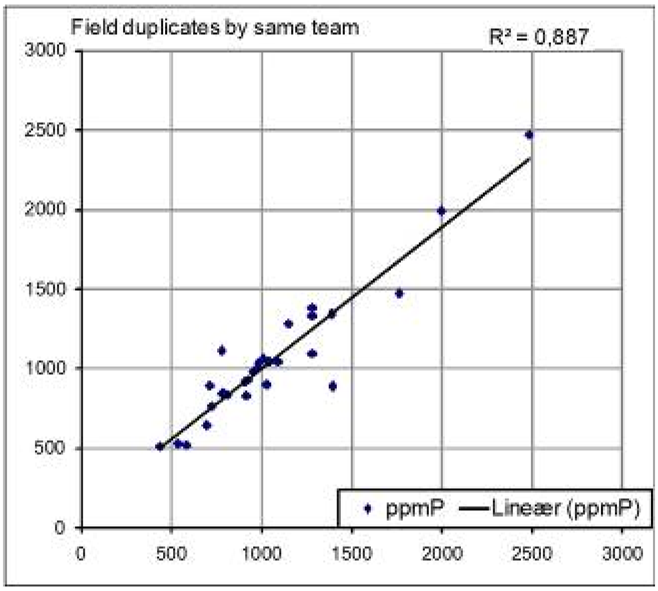

ppmMo
6
5
4
3
2
1
0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

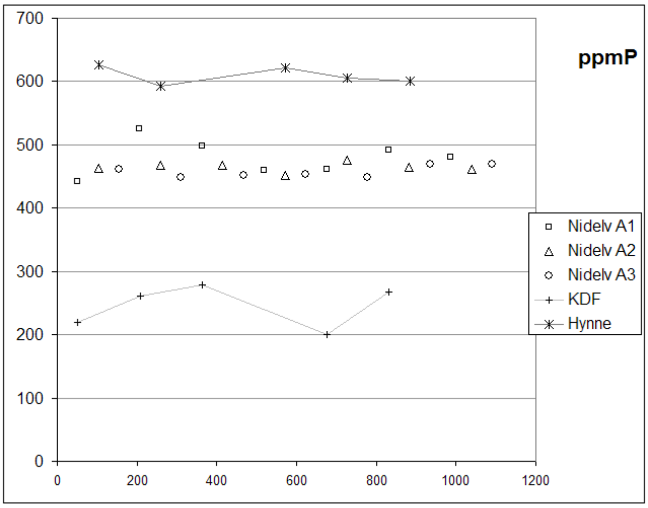

Field duplicates by same team
R² = 0,8227
1200
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
ppmNa
Linear (ppmNa)

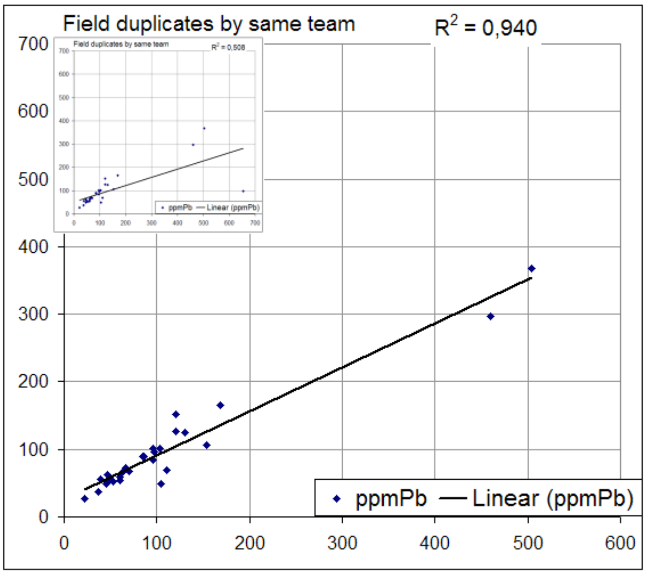

ppmNa
8000
7000
6000
5000
4000
3000
2000
1000
0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne


Field duplicates by same team
R² = 0,730
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
ppmNi
Lineær (ppmNi)


ppmNi
45,0
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne


Field duplicates by same team
R² = 0,887
3000
2500
2000
1500
1000
500
0
0
500
1000
1500
2000
2500
3000
ppmP
Lineær (ppmP)


ppmP
700
600
500
400
300
200
100
0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne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R² = 0,940
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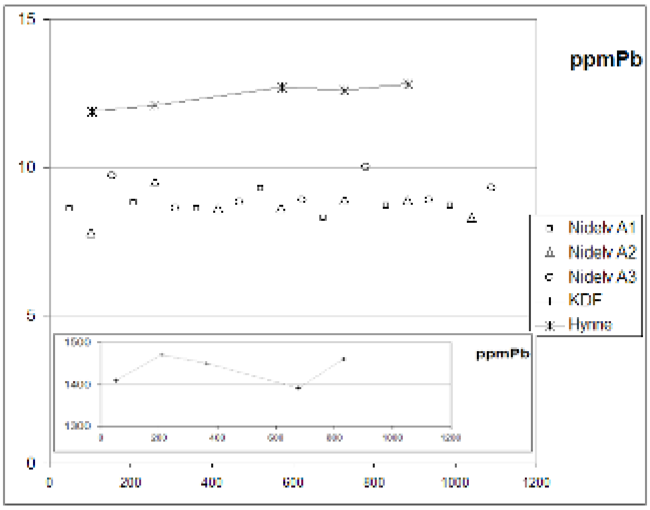
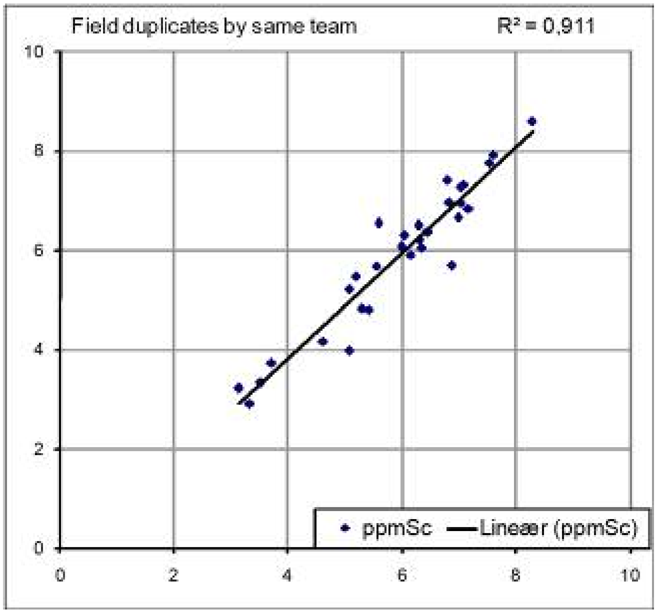
600
500
400
300
200
100
0
0
100
200
300
400
500
600
ppmPb
Linear (ppmPb)
Field duplicates by same team
R² = 0,508
ppmPb
Linear (ppmPb)


ppmPb
15
10
5
0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne
ppmPb
1500
1400
1300
0
200
400
600
800
1000
1200


Field duplicates by same team
R² = 0,911
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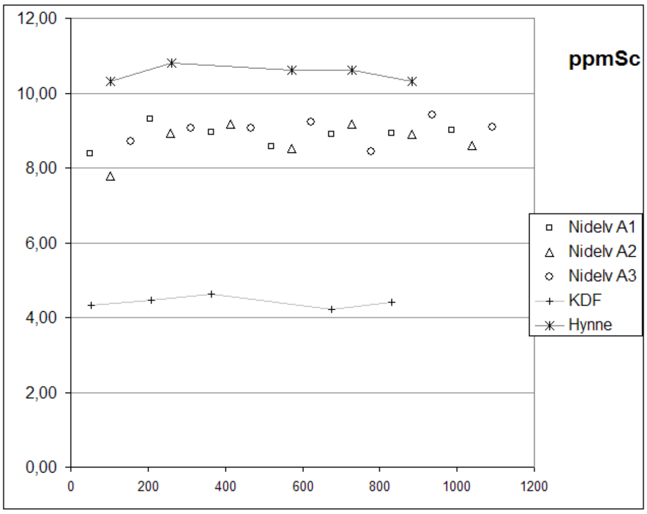
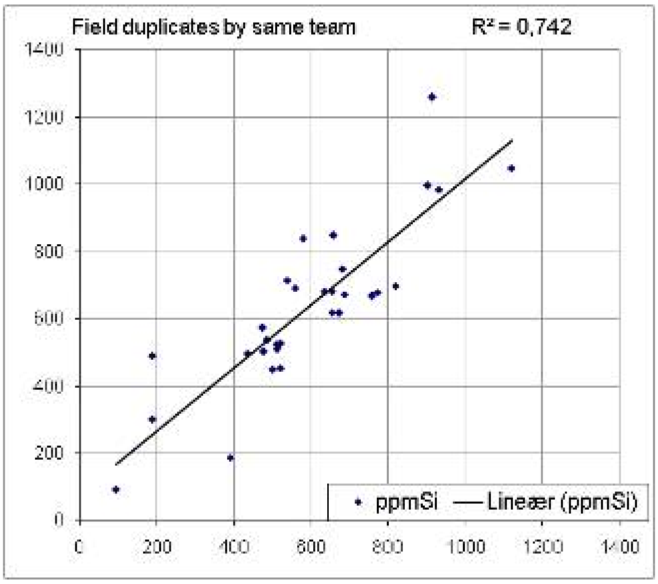
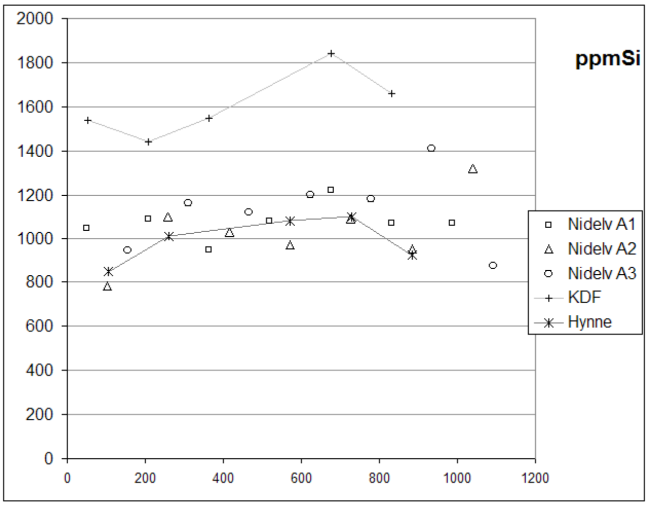
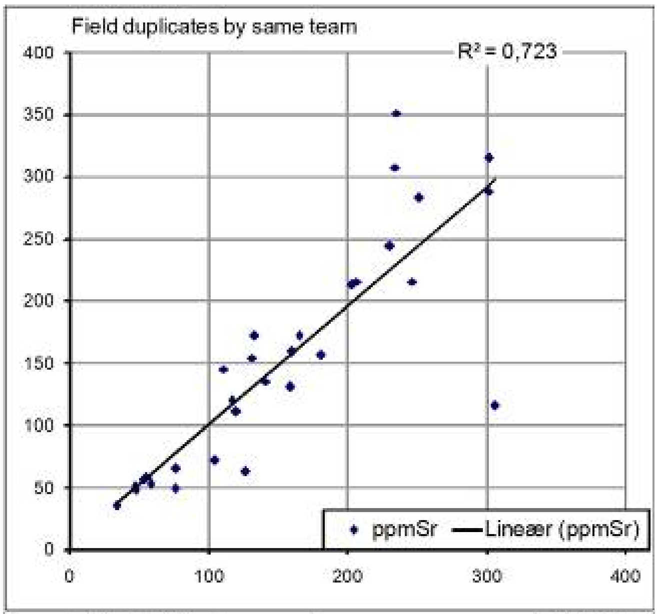
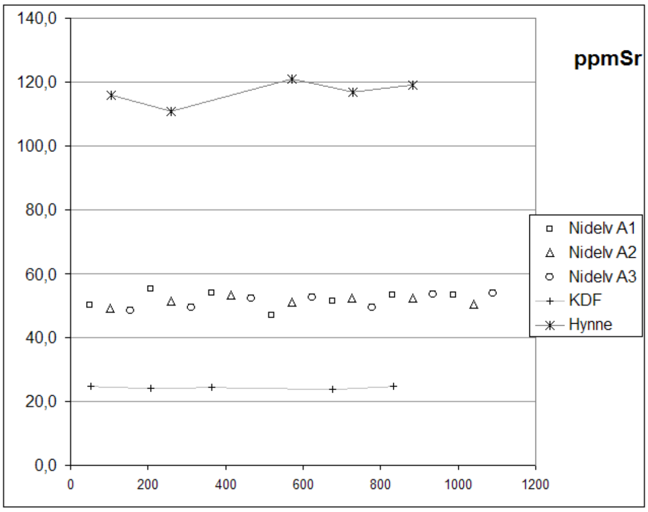
8
6
4
2
0
0
2
4
6
8
10
ppmSc
Lineær (ppmSc)

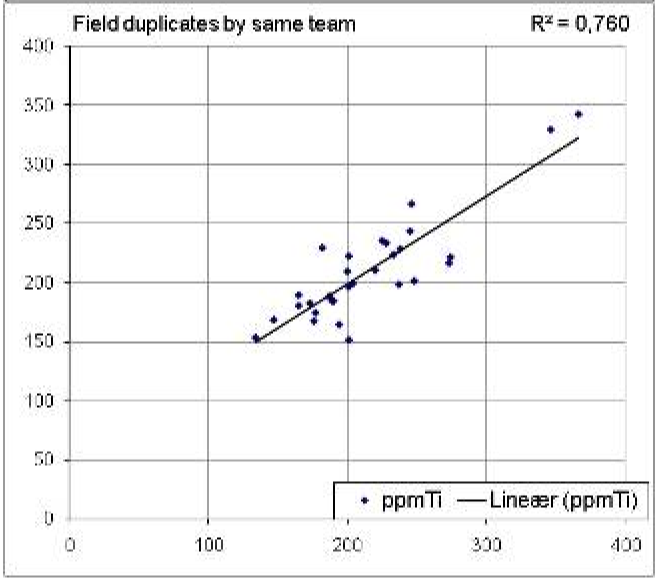

ppmSc
12,00
10,00
8,00
6,00
4,00
2,00
0,00
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

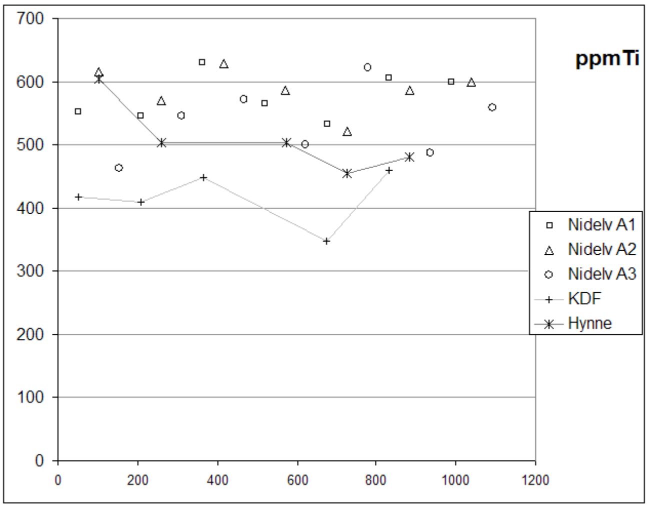

Field duplicates by same team
R² = 0,742
1400
1200
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
1400
ppmSi
Lineær (ppmSi)

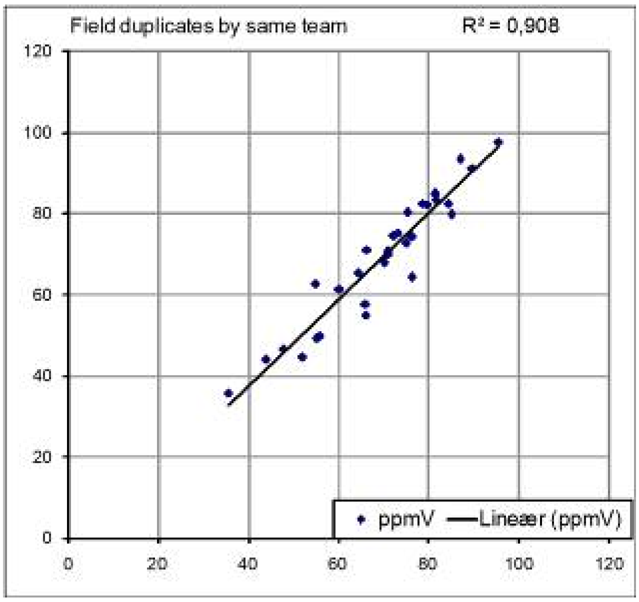

ppmSi
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

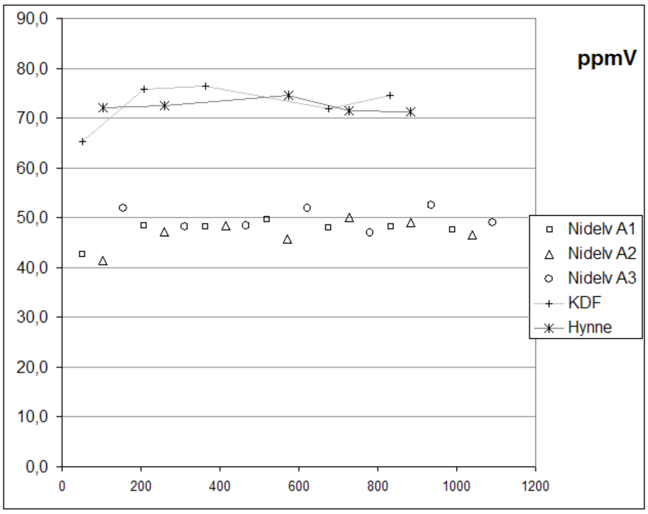

Field duplicates by same team
R² = 0,723
400
350
300
250
200
150
100
50
0
0
100
200
300
400
ppmSr
Lineær (ppmSr)

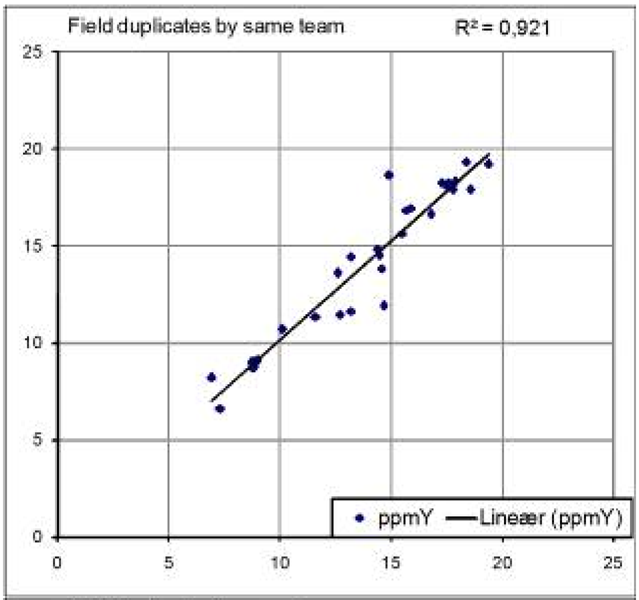

ppmSr
140,0
120,0
100,0
80,0
60,0
40,0
20,0
0,0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

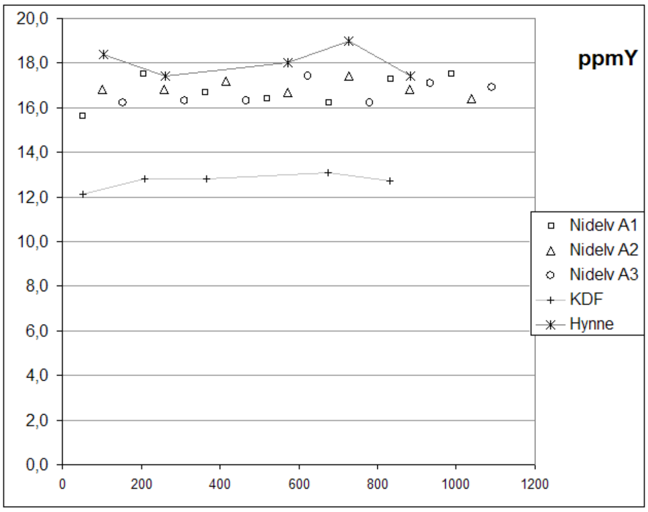

Field duplicates by same team
R² = 0,760
400
350
300
250
200
150
100
50
0
0
100
200
300
400
ppmTi
Lineær (ppmTi)

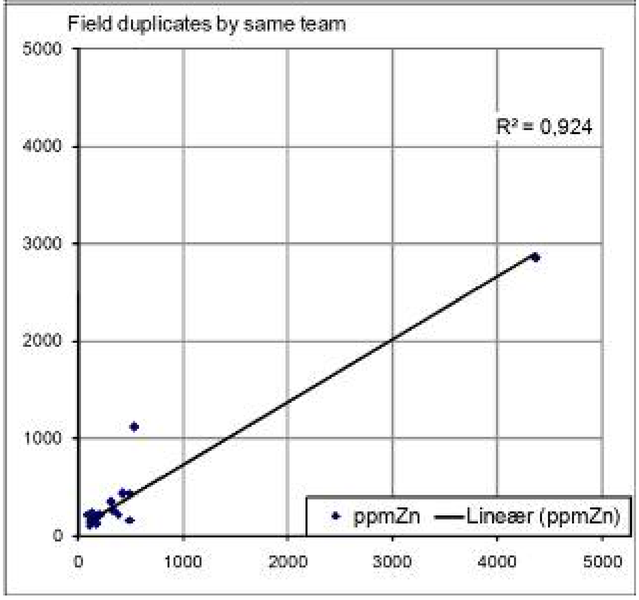

ppmTi
700
600
500
400
300
200
100
0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

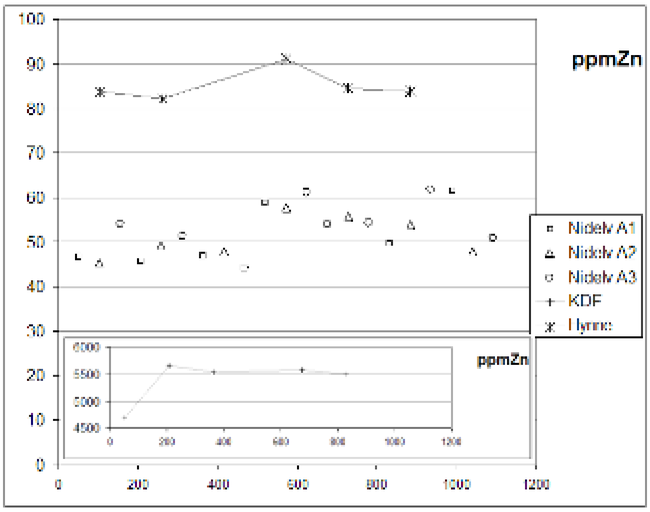

Field duplicates by same team
R² = 0,908
0
20
40
60
80
100
120
ppmV
Lineær (ppmV)

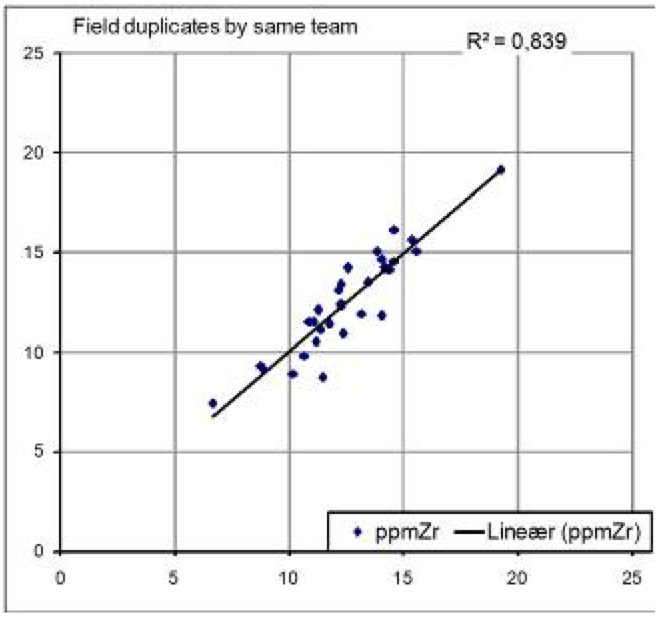

ppmV
0,0
10,0
20,0
30,0
40,0
50,0
60,0
70,0
80,0
90,0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

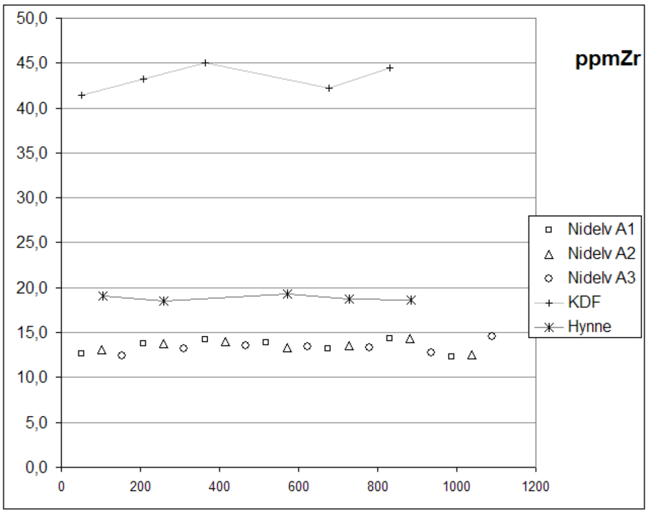

Field duplicates by same team
R² = 0,921
0
5
10
15
20
25
ppmY
Lineær (ppmY)

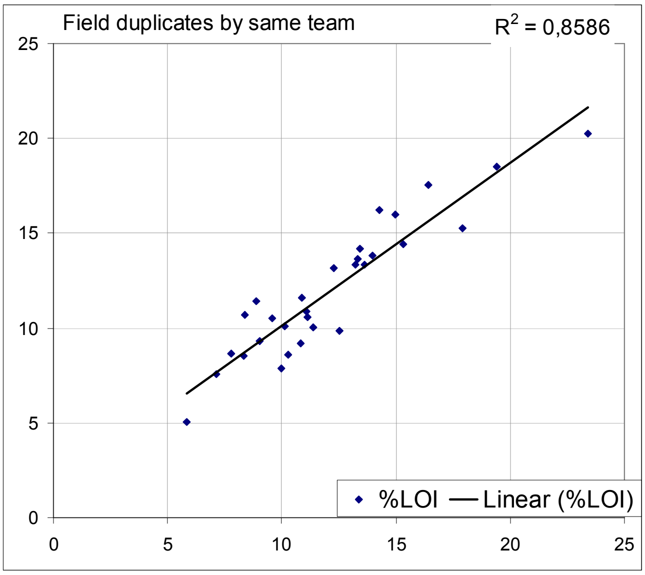

ppmY
0,0
2,0
4,0
6,0
8,0
10,0
12,0
14,0
16,0
18,0
20,0
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne


Field duplicates by same team
R² = 0,924
0
1000
2000
3000
4000
5000
ppmZn
Lineær (ppmZn)


ppmZn
0
10
20
30
40
50
60
70
80
90
100
0
200
400
600
800
1000
1200
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne
ppmZn
4500
5000
5500
6000


Field duplicates by same team
R² = 0,839
25
20
15
10
5
0
0
5
10
15
20
25
ppmZr
Lineær (ppmZr)


50,0
45,0
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
0
200
400
600
800
1000
1200
ppmZr
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne


Field duplicates by same team
R² = 0,8586
25
20
15
10
5
0
0
5
10
15
20
25
%LOI
Linear (%LOI)

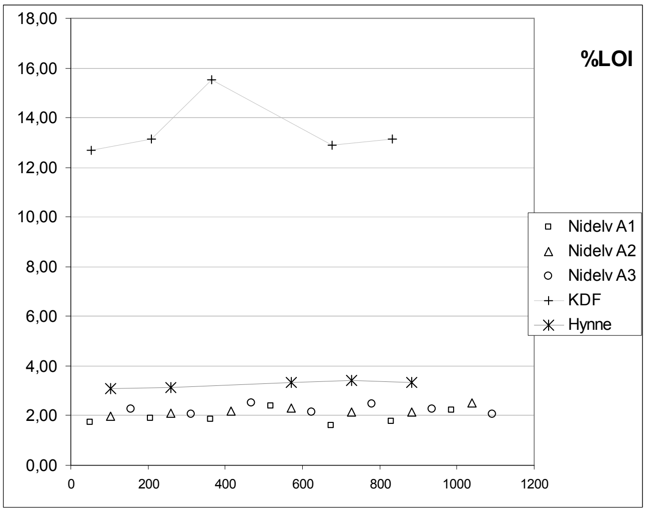

18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
0
200
400
600
800
1000
1200
%LOI
Nidelv A1
Nidelv A2
Nidelv A3
KDF
Hynne

Table A1. Summary of analytical data. certified reference material MESS-3 (NRC-CNRC). Certificate values are total content.

Element	Mean	SD	%RSD	N	Median	Certificate value	Rel. dev.% (vs. certificate)
Si	516.2	208.3	40.4 %	52	500.0	270000	-99.8 %
Al	68475	3940	5.8 %	52	67768	85900	-20.3 %
Fe	38043	806	2.1 %	52	38104	43400	-12.3 %
Ti	171	25	14.5 %	52	176	4400	-96.1 %
Mg	16879	343	2.0 %	52	16875	16000	5.5 %
Ca	14126	265	1.9 %	52	14111	14700	-3.9 %
Na	12729	207	1.6 %	52	12755	16000	-20.4 %
K	20272	1683	8.3 %	52	20008	26000	-22.0 %
Mn	297	5	1.7 %	52	297	324	-8.4 %
P	1064	22	2.1 %	52	1063	1200	-11.4 %
Cu	26.0	0.7	2.7 %	52	25.9	33.9	-23.2 %
Zn	150	6	4.0 %	52	150	159	-5.8 %
Pb	16.5	0.6	3.6 %	52	16.4	21.1	-21.9 %
Ni	40.1	1.2	3.1 %	52	39.9	46.9	-14.4 %
Co	11.1	0.2	1.9 %	52	11.1	14.4	-23.2 %
V	183	8	4.6 %	52	182	243	-24.6 %
Mo	0.1	0.2	362.9 %	52	0.1	2.78	-97.8 %
Cd	0.3	0.0	15.6 %	52	0.30	0.24	29.4 %
Cr	75.0	3.8	5.0 %	52	74.1	105	-28.6 %
Ba	748	38	5.1 %	52	737	-	-
Sr	102	5	5.0 %	52	102	129	-20.7 %
Zr	11.7	1.7	14.3 %	52	11.5	-	-
B	115	5	4.6 %	52	116	-	-
Be	1.8	0.1	3.6 %	52	1.8	2.3	-20.2 %
Li	70.9	1.3	1.8 %	52	70.9	73.6	-3.7 %
Sc	10.9	0.5	5.0 %	52	10.8	-	-
Ce	40.7	2.9	7.1 %	52	39.8	-	-
La	23.0	1.4	6.2 %	52	22.4	-	-
Y	13.8	0.3	2.5 %	52	13.7	-	-
As	15.1	0.9	5.7 %	52	15.2	21.2	28.8 %

Table A2. Summary of analytical data. certified reference material NIST2709 (NIST). Certificate values are total content.

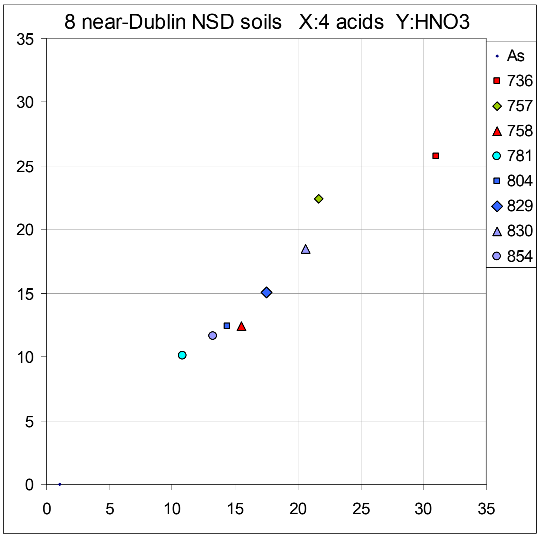
Element	Mean	SD	%RSD	N	Median	Certificate value	Rel. dev. % (vs. certificate)
Si	491	65	13.2 %	6	476	296600	-99.8 %
Al	47267	1050	2.2 %	6	47800	75000	-37.0 %
Fe	29733	987	3.3 %	6	29850	35000	-15.0 %
Ti	341	19	5.7 %	6	335	3420	-90.0 %
Mg	15167	137	0.9 %	6	15200	15100	0.4 %
Ca	15133	197	1.3 %	6	15100	18900	-19.9 %
Na	1275	48	3.7 %	6	1270	11600	-89.0 %
K	7910	244	3.1 %	6	7925	20300	-61.0 %
Mn	450	13	2.8 %	6	444	538	-16.4 %
P	518	6	1.2 %	6	517	620	-16.4 %
Cu	28.6	0.7	2.6 %	6	28.7	34.6	-17.4 %
Zn	96.0	2.2	2.3 %	6	95.6	106	-9.5 %
Pb	11.3	0.4	3.8 %	6	11.3	18.9	-40.0 %
Ni	69.5	0.8	1.2 %	6	69.3	88	-21.0 %
Co	10.4	0.2	2.2 %	6	10.3	13.4	-22.5 %
V	79.4	1.5	1.9 %	6	79.8	112	-29.1 %
Mo	-	-	-	-	-	-	-
Cd	0.4	0.0	6.3 %	6	0.3	0.38	-6.1 %
Cr	88.9	3.0	3.4 %	6	90.1	130	-31.6 %
Ba	492	8	1.6 %	6	494	968	-49.2 %
Sr	119	2	1.4 %	6	119	231	-48.6 %
Zr	8.2	0.4	4.7 %	6	8.4	-	-
B	47.7	0.5	1.1 %	6	48.0	-	-
Be	1.1	0.0	4.1 %	6	1.1	-	-
Li	52.7	1.1	2.0 %	6	53.0	-	-
Sc	9.0	0.1	1.2 %	6	9.0	-	-
Ce	35.9	0.4	1.0 %	6	35.9	-	-
La	19.0	0.3	1.6 %	6	18.9	-	-
Y	11.0	0.1	0.6 %	6	11.0	-	-
As	9.1	0.5	5.7 %	6	9.2	17.7	-48.9 %

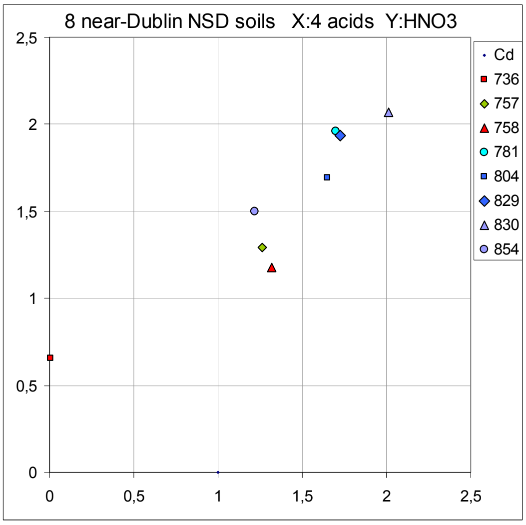
Table A3. Summary of analytical data. certified reference material SO2 (CCRMP. CANMET Mining and Mineral Sciences Laboratories). Certificate values are total content.

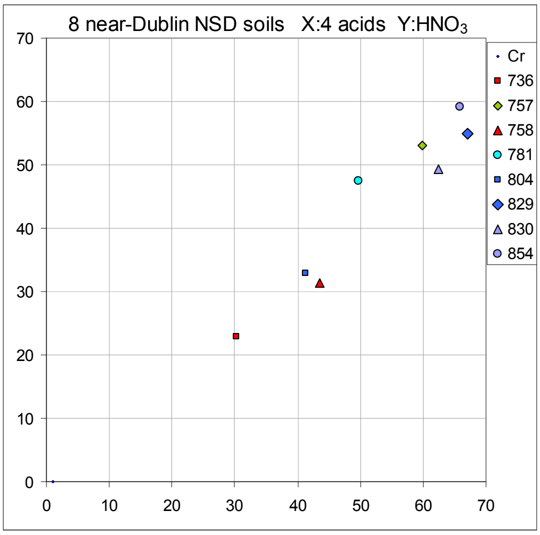
Element	Mean	SD	%RSD	N	Median	Certificate value	Rel. dev. % (vs. certificate)
Si	907	30	3.3 %	6	909	249922	-99.6 %
Al	26000	410	1.6 %	6	26050	80700	-67.8 %
Fe	34467	547	1.6 %	6	34500	55600	-38.0 %
Ti	410	32	7.8 %	6	420	8600	-95.2 %
Mg	2992	85	2.9 %	6	2960	5400	-44.6 %
Ca	5673	80	1.4 %	6	5645	19600	-71.1 %
Na	963	37	3.8 %	6	960	19000	-94.9 %
K	1153	45	3.9 %	6	1145	24500	-95.3 %
Mn	305	9	3.0 %	6	306	720	-57.6 %
P	2363	304	12.9 %	6	2525	3000	-21.2 %
Cu	3.45	0.78	22.5 %	6	3.4	7.0	-50.7 %
Zn	83.5	2.44	2.9 %	6	83.9	124.0	-32.7 %
Pb	6.45	0.14	2.1 %	6	6.45	21.0	-69.3 %
Ni	4.5	0.73	16.3 %	6	4.55	8.0	-43.8 %
Co	4.41	0.11	2.6 %	6	4.42	9.00	-51.1 %
V	40.6	0.91	2.2 %	6	40.6	64.0	-36.6 %
Mo	-	-	-	-	-	-	-
Cd	-	-	-	-	-	-	-
Cr	8.04	0.50	6.3 %	6	7.87	16.00	-49.8 %
Ba	50.18	0.69	1.4 %	6	50.30	966.0	-94.8 %
Sr	14.25	0.23	1.6 %	6	14.20	340.0	-95.8 %
Zr	16.25	1.64	10.1 %	6	16.70	-	-
B	-	-	-	-	-	-	-
Be	0.43	0.04	9.7 %	6	0.41	-	-
Li	4.57	0.23	5.1 %	6	4.64	-	-
Sc	5.88	0.11	1.9 %	6	5.85	-	-
Ce	95.0	1.3	1.3 %	6	95.2	-	-
La	34.7	0.551	1.6 %	6	34.8	-	-
Y	28.93	0.38	1.3 %	6	29.1	-	-
As	2.08	0.40	19.4 %	5	1.9	-	-

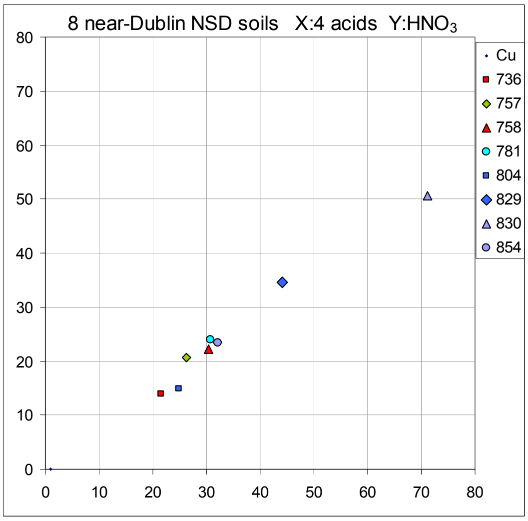
Appendix B – Comparison of geochemical concentrations for NSDB soil samples

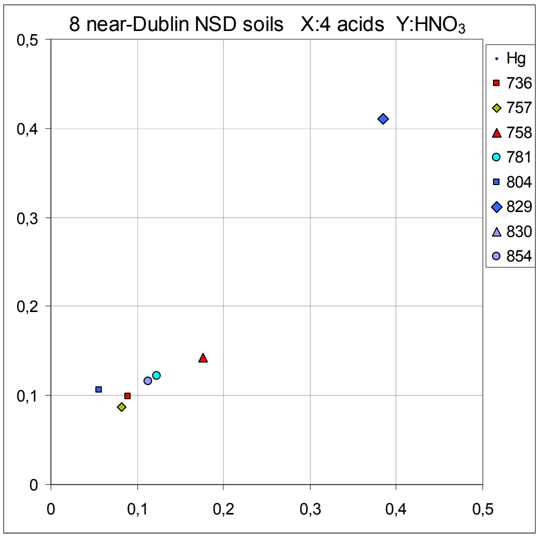
Scatter plots comparing concentrations of results for NSDB samples in original survey and SURGE survey

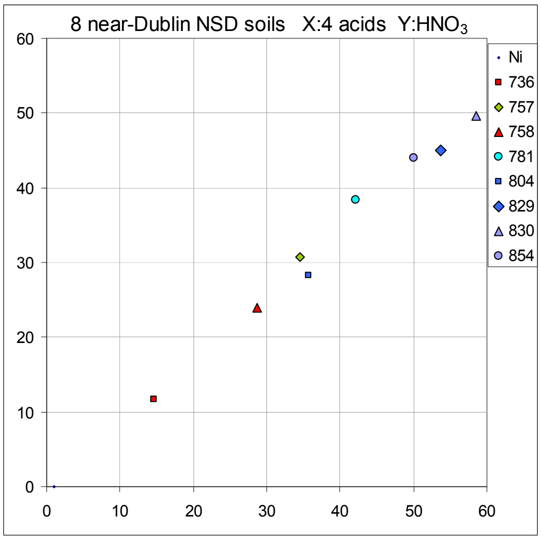


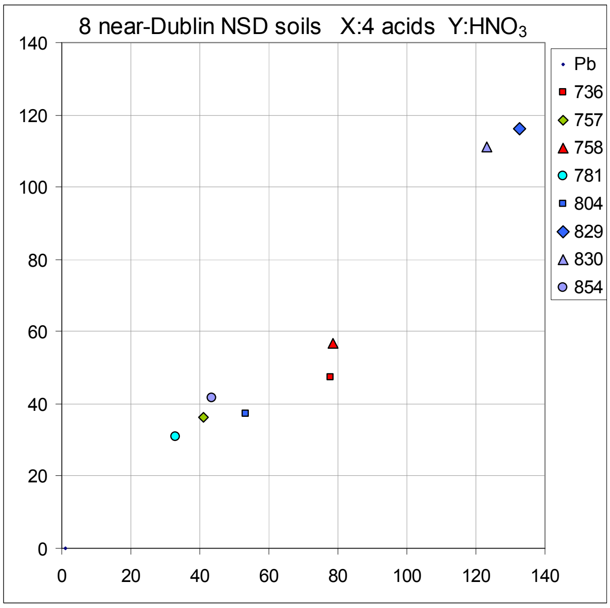


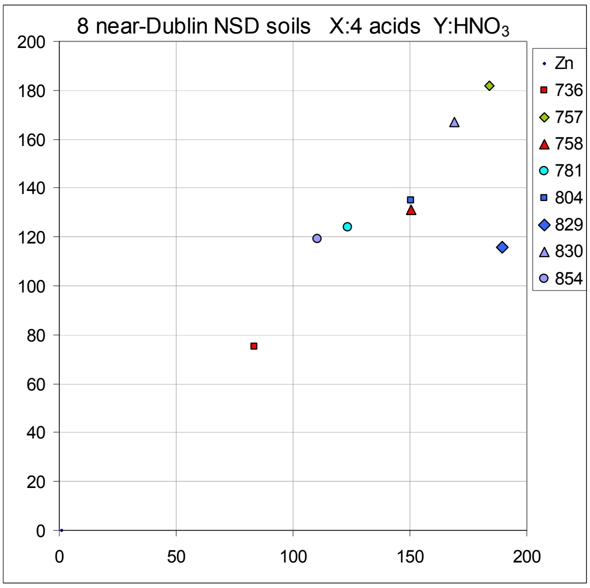












Element	Correlation coefficient
Al	-0,09
Ca	0,99
Fe	0,95
K	-0,56
Mg	0,96
Mn	0,95
Na	-0,83
P	0,84
Ti	0,45
As	**0,96**
Ba	0,38
Cd	**0,93**
Ce	0,83
Co	0,97
Cr	**0,96**
Cu	**0,99**
Hg	**0,99**
La	0,87
Li	1,00
Mo	0,82
Ni	**0,99**
Pb	**0,97**
Sc	0,98
Sr	0,88
V	0,97
Y	0,97
Zn	**0,94**

Table B1 Correlation coefficients for all the 27 common variables. Scatter plots are shown above for the elements indicated in bold. Elements indicated in red are (except for Ti) as expected due to difference in extraction capabilities between the acids used on silicate materials.

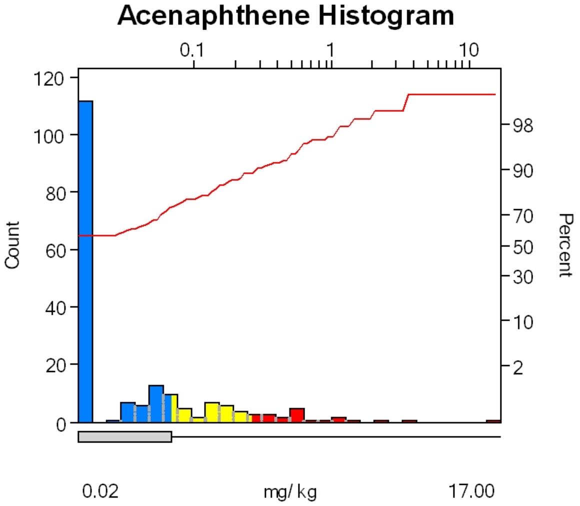
Appendix C – Individual PAH compound maps

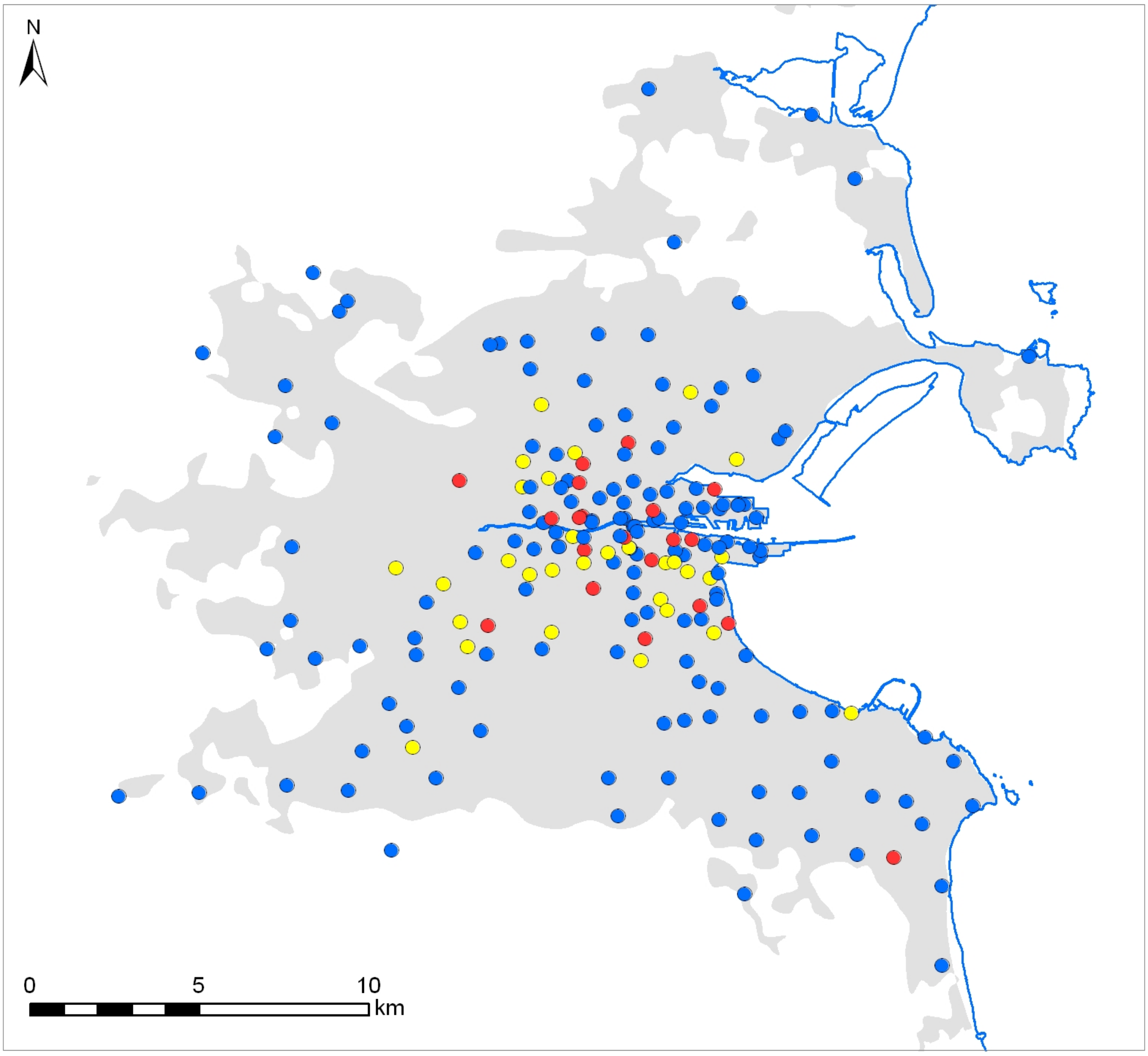
Dublin SURGE Project

Acenaphthene - topsoil

Percentile		mg/kg
Min - 75th	🔵	<0.03 - 0.07
75th - 90th	🟡	0.07 - 0.27
90th - max	🔴	0.27 - 17

Median = <0.03 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg



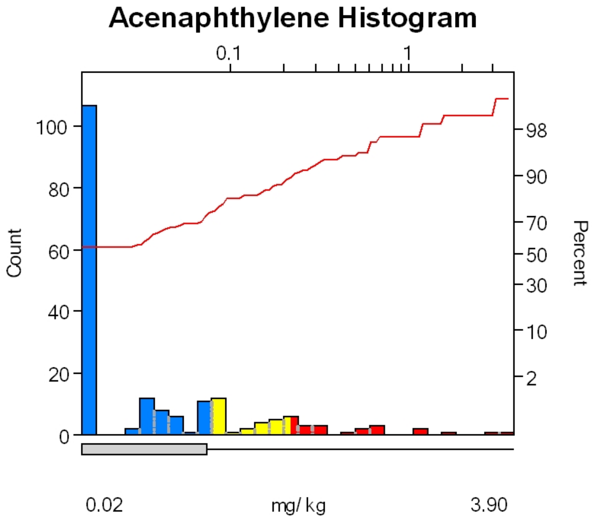


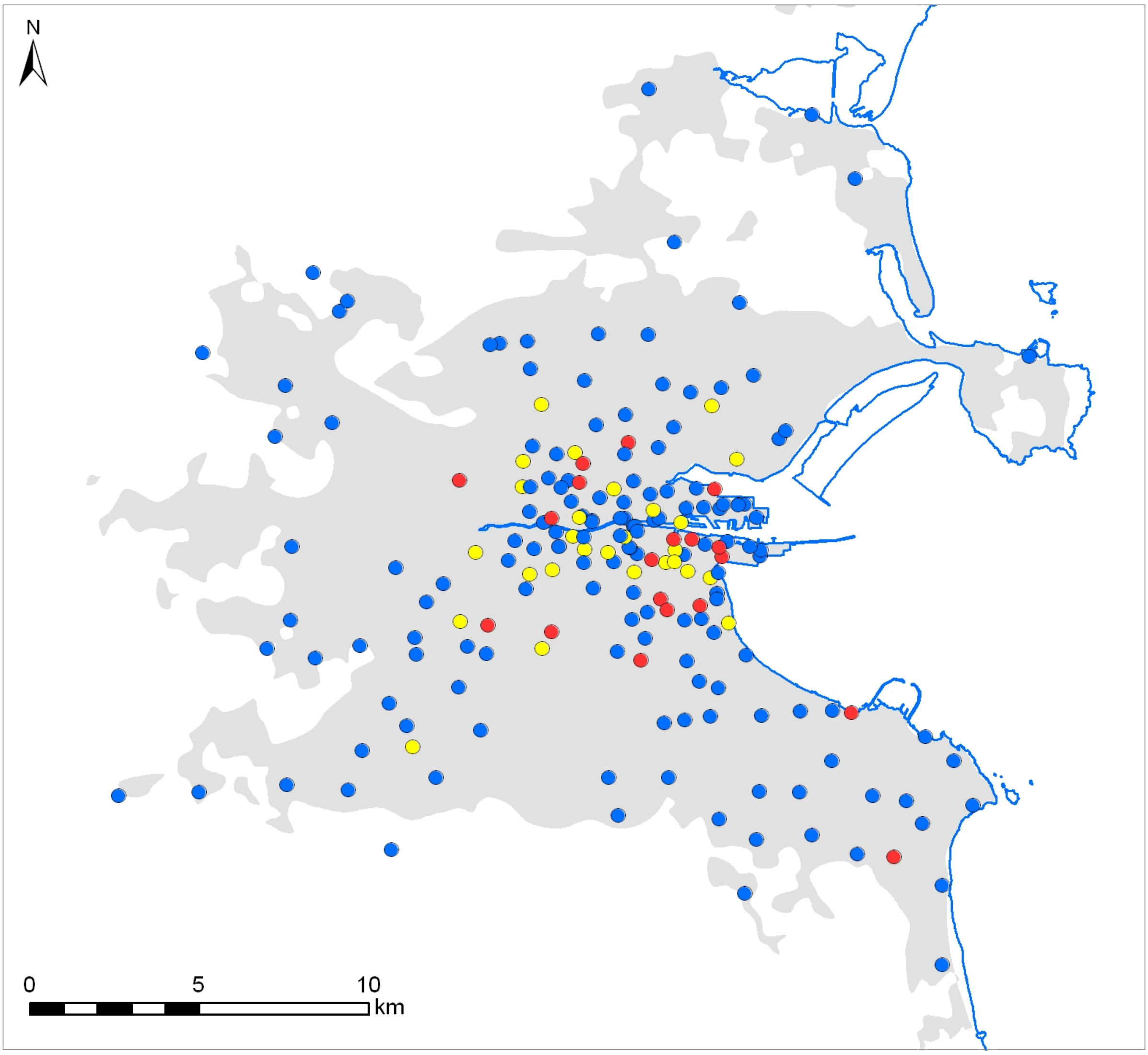
Dublin SURGE Project

Acenaphthylene - topsoil

Percentile		**mg/kg**
Min - 75th	🔵	<0.03 - 0.08
75th - 90th	🟡	0.08 - 0.22
90th - max	🔴	0.22 - 3.9

Median = <0.03 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg





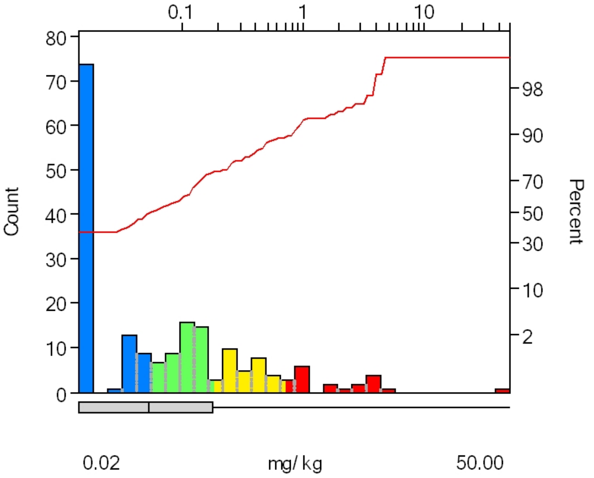
Dublin SURGE Project

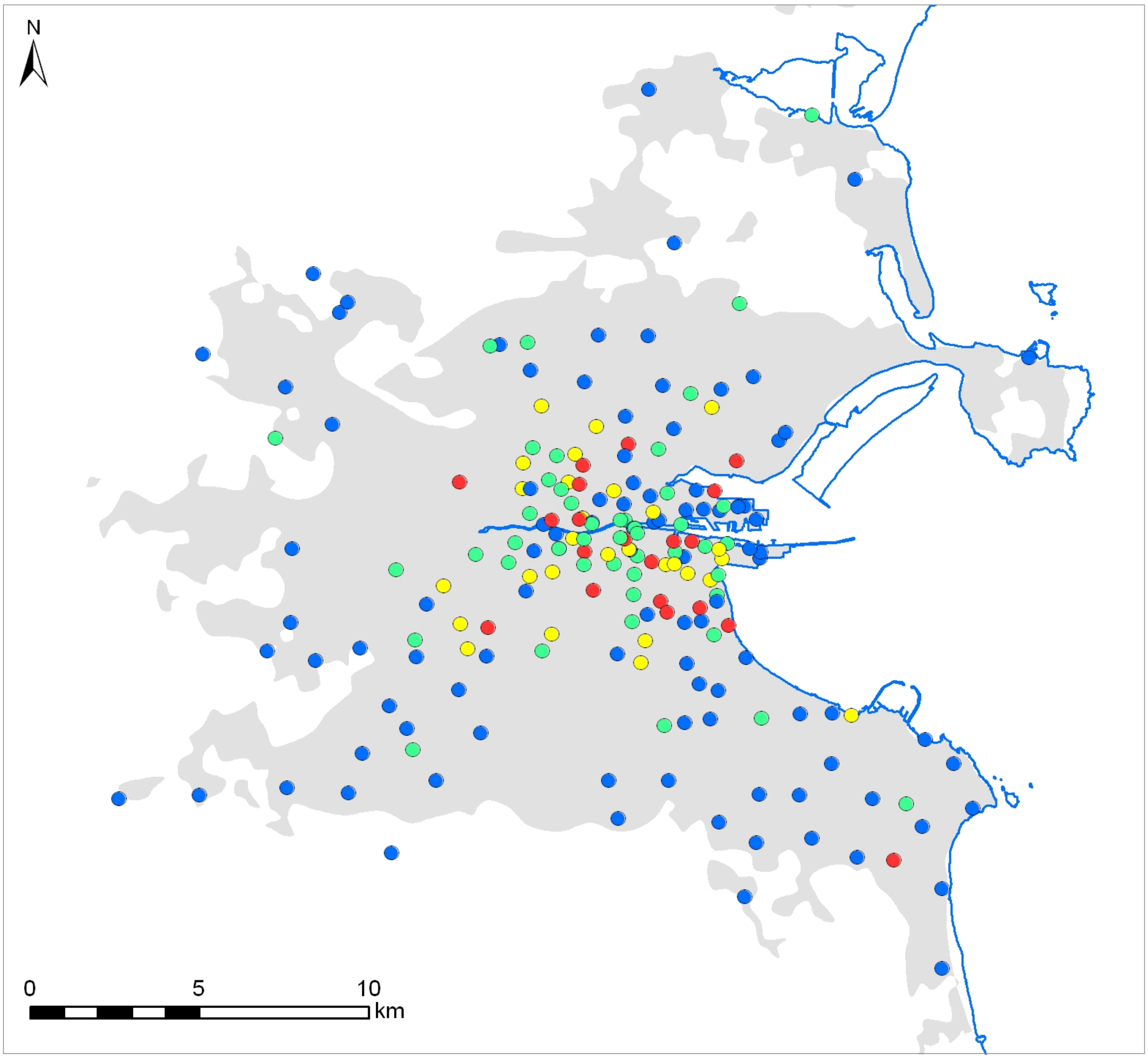
Anthracene - topsoil

Percentile		mg/kg
Min - 50th	🔵	<0.03 - 0.06
50th - 75th	🟢	0.06 - 0.19
75th - 90th	🟡	0.19 - 0.73
90th - max	🔴	0.73 - 50

Median = 0.06 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg

Anthracene Histogram



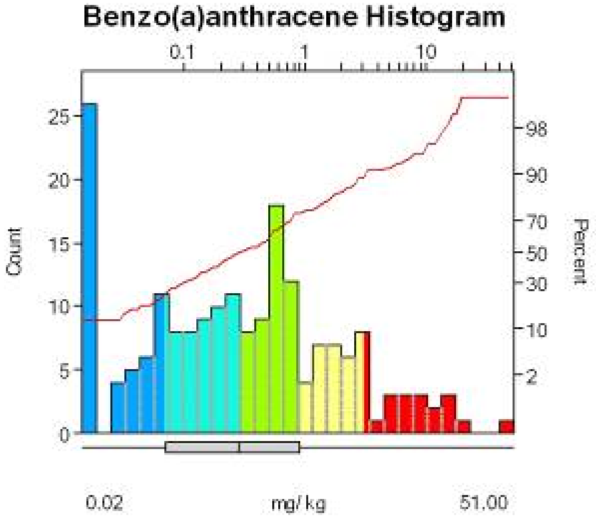


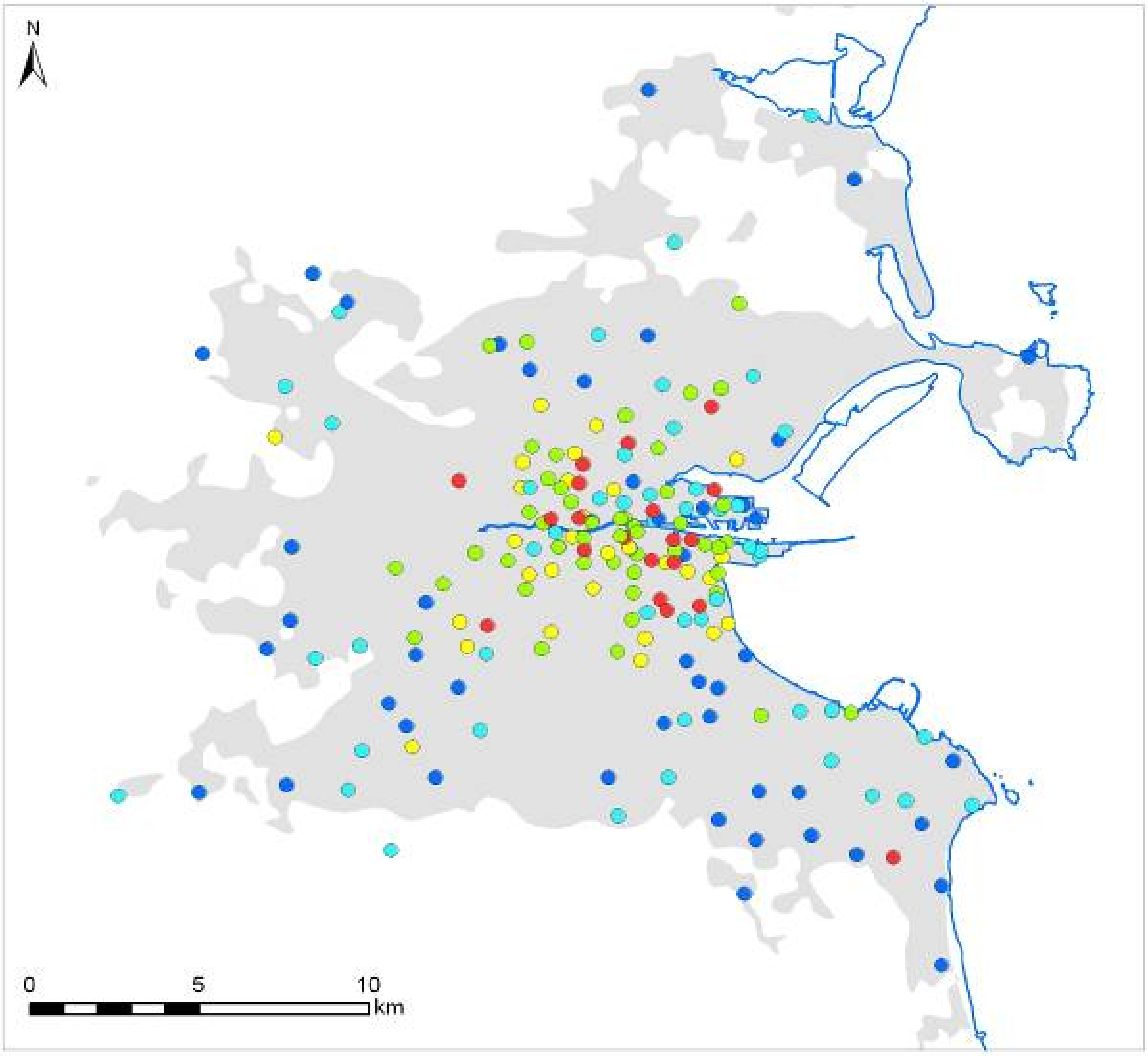
Dublin SURGE Project

Benzo(a)anthracene - topsoil

Percentile		mg/kg
Min - 25th	●	<0.03 - 0.07
25th - 50th	●	0.07 - 0.29
50th - 75th	●	0.29 - 0.92
75th - 90th	●	0.92 - 3.01
90th - max	●	3.01 - 51

Median = 0.29 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg



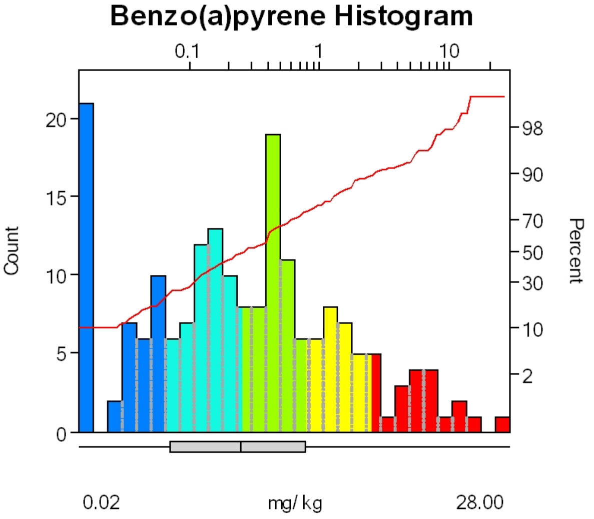


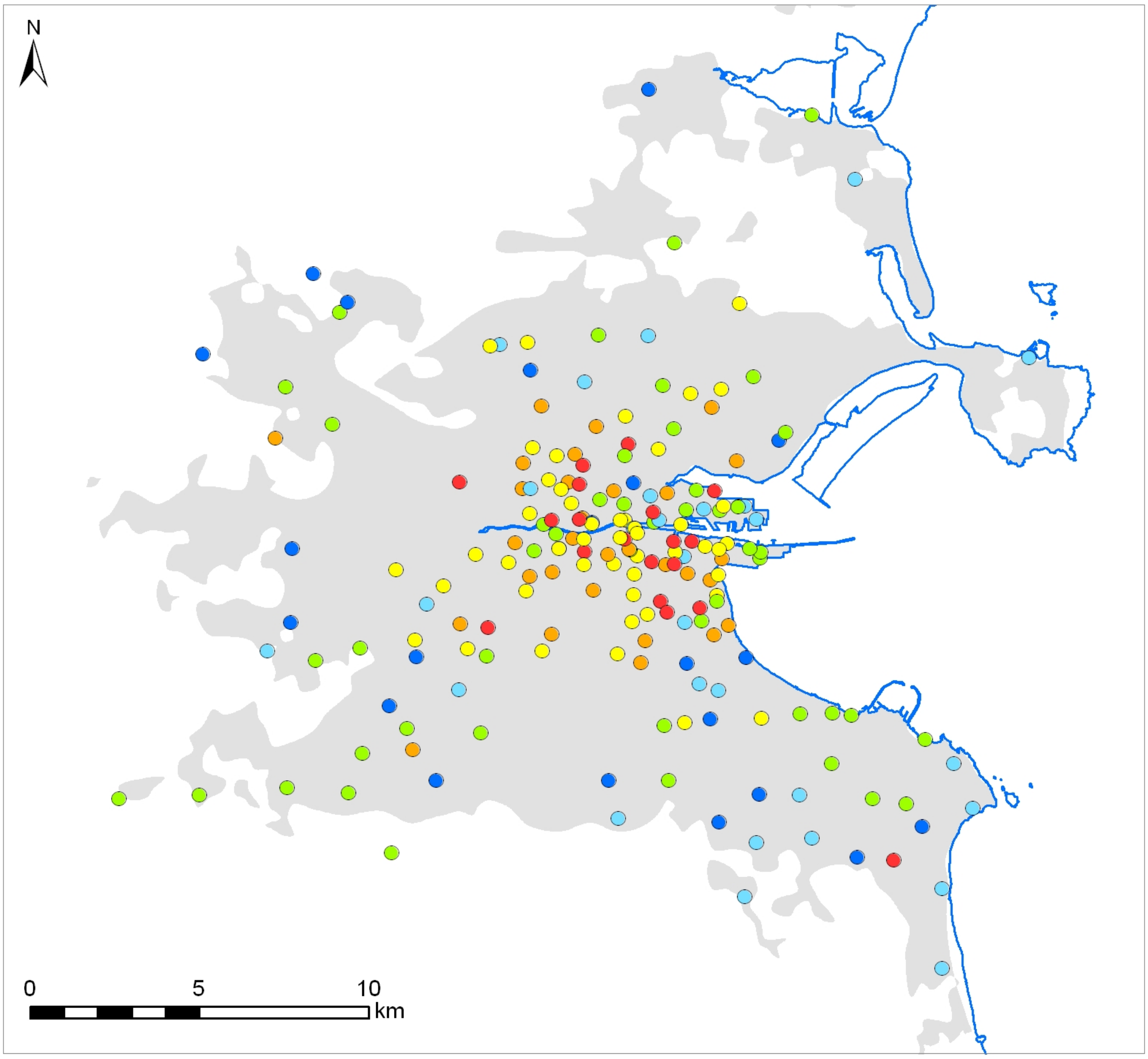
Dublin SURGE Project

Benzo(a)pyrene - topsoil

Percentile		mg/kg
Min - 25th	●	<0.03 - 0.07
25th - 50th	●	0.07 - 0.26
50th - 75th	●	0.26 - 0.79
75th - 90th	●	0.79 - 2.5
90th - max	●	2.5 - 28

Median = 0.26 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg





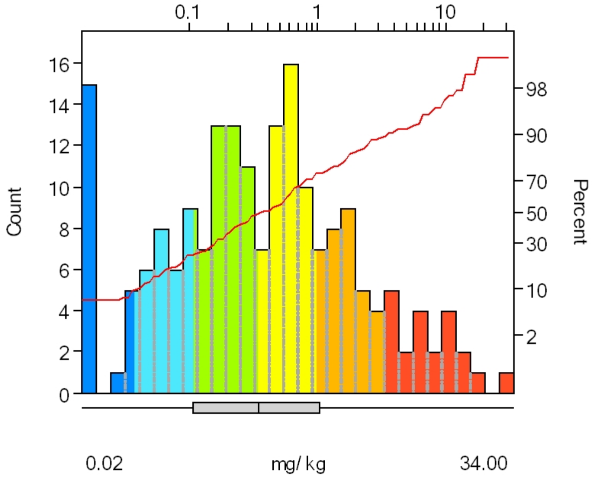
Dublin SURGE Project

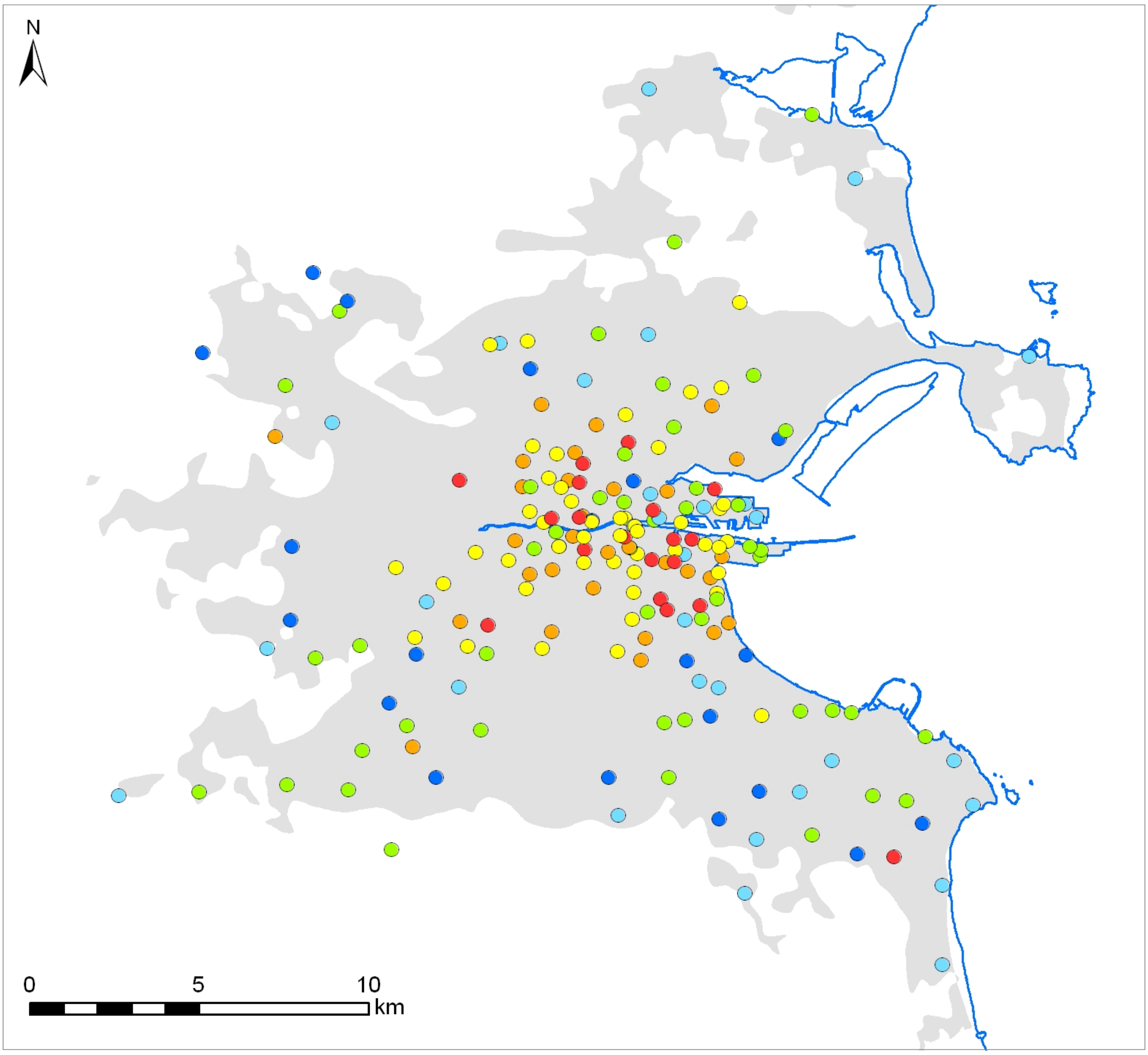
Benzo(b)fluoranthene - topsoil

Percentile		mg/kg
Min - 10th	●	<0.03 - 0.04
10th - 25th	●	0.04 - 0.11
25th - 50th	●	0.11 - 0.36
50th - 75th	●	0.36 - 1.08
75th - 90th	●	1.08 - 3.40
90th - max	●	3.40 - 34

Median = 0.36 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg

Benzo(b)fluoranthene Histogram



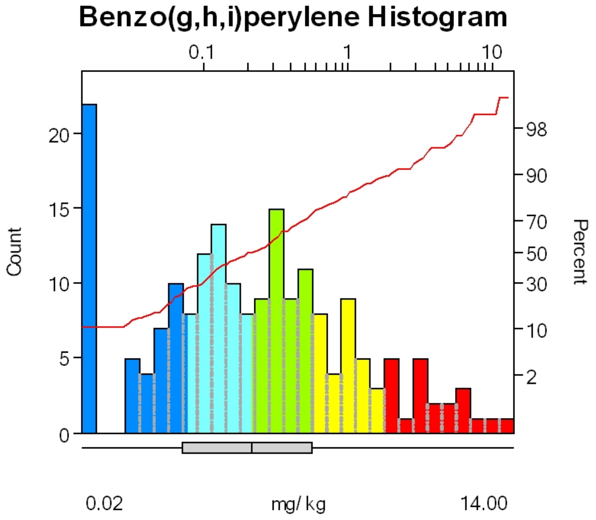


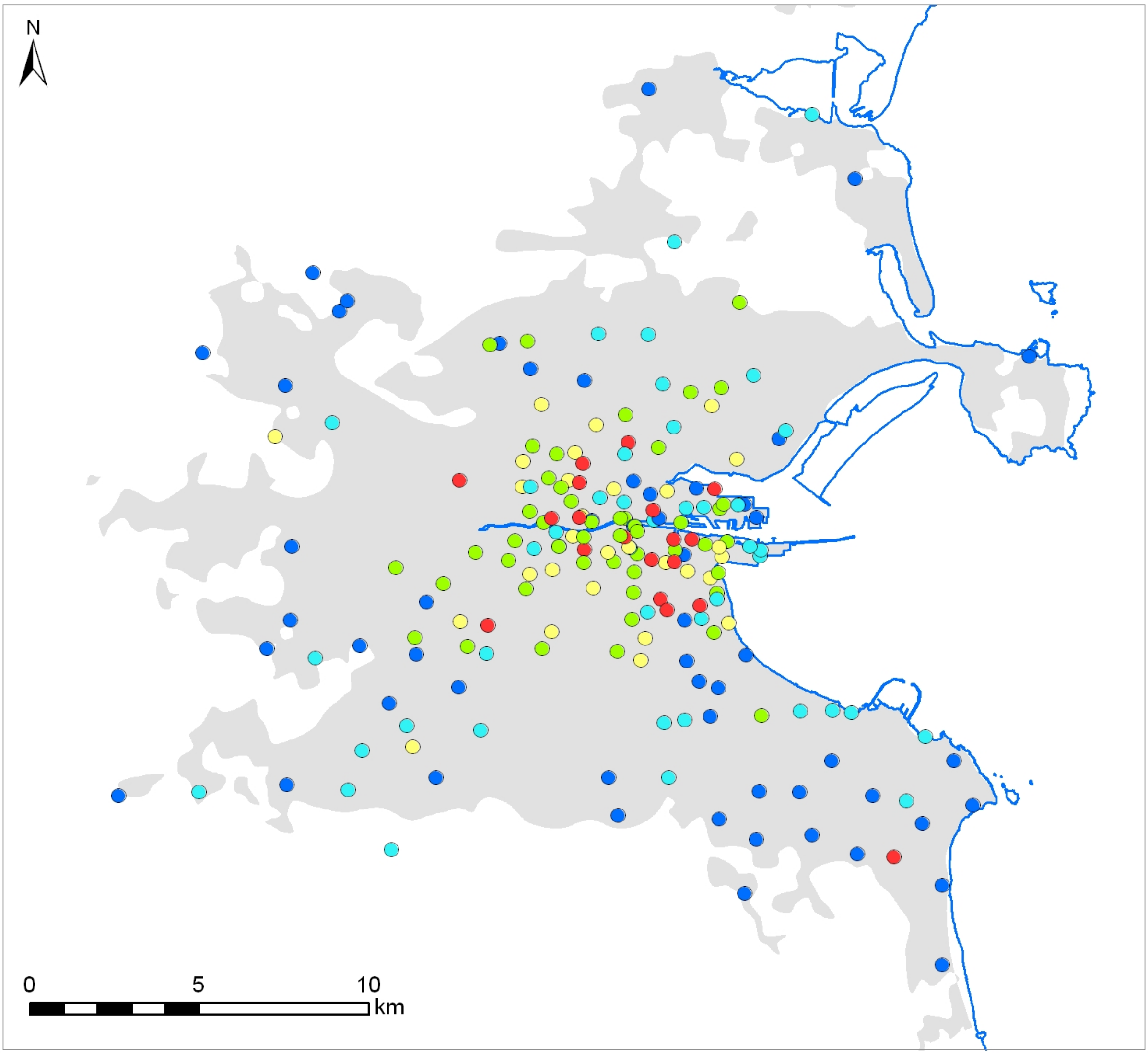
Dublin SURGE Project

Benzo(g,h,i)perylene - topsoil

Percentile		mg/kg
Min - 25th	●	<0.03 - 0.08
25th - 50th	●	0.08 - 0.22
50th - 75th	●	0.22 - 0.59
75th - 90th	●	0.59 - 1.8
90th - max	●	1.8 - 14

Median = 0.22 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg


Benzo(g,h,i)perylene Histogram

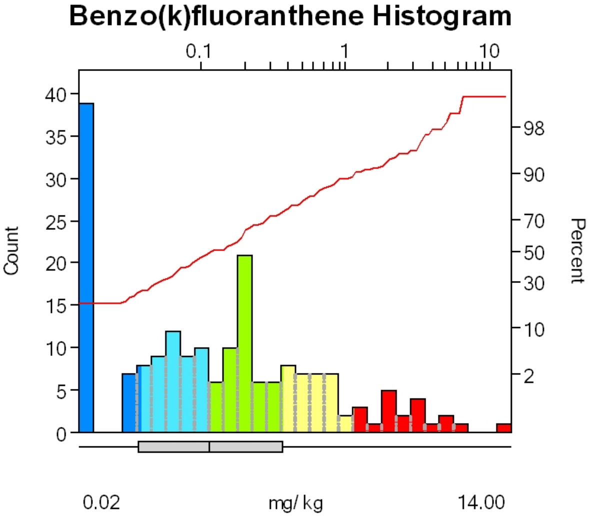


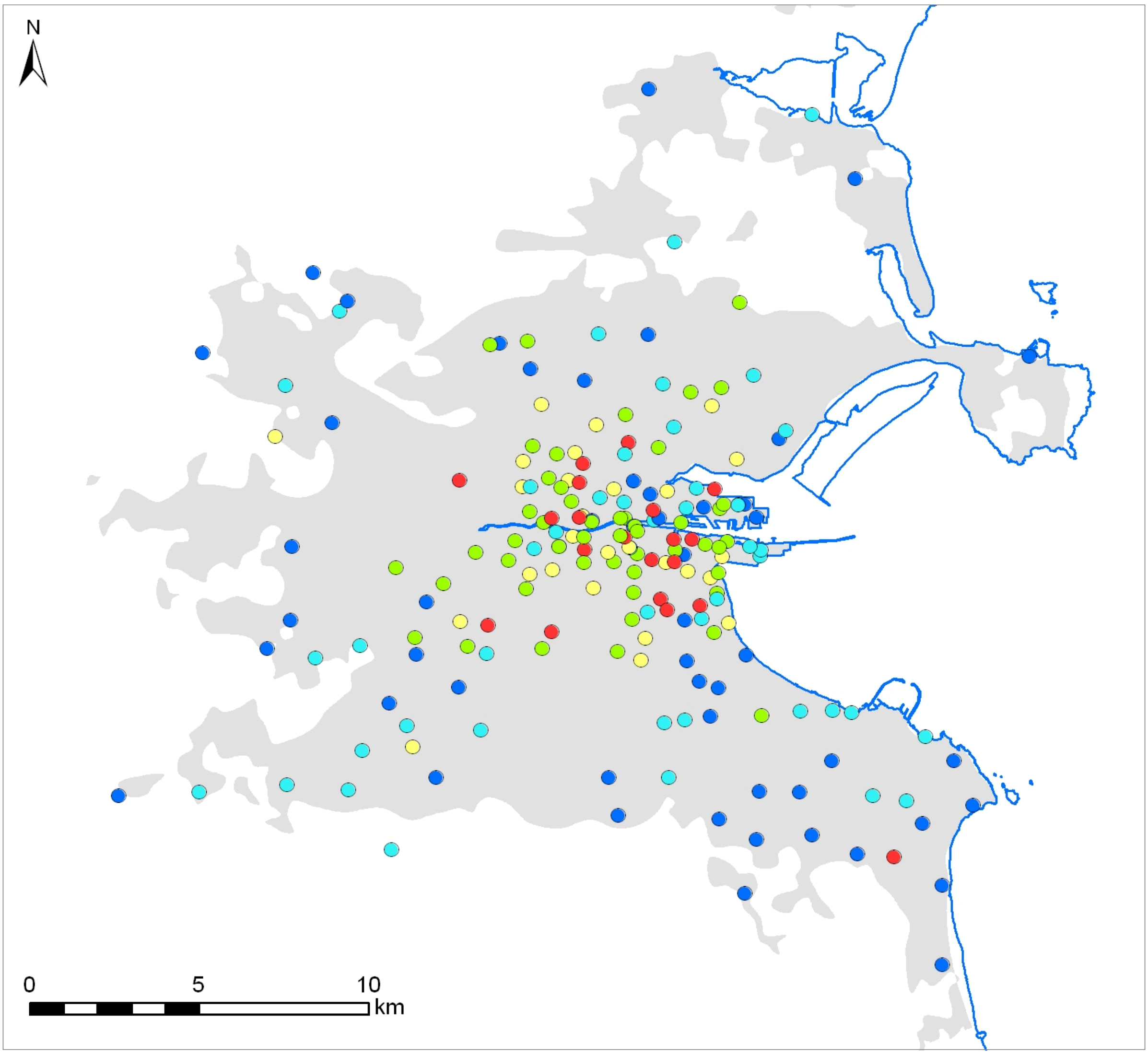
Dublin SURGE Project

Benzo(k)fluoranthene - topsoil

Percentile		mg/kg
Min - 25th	●	<0.03 - 0.08
25th - 50th	●	0.08 - 0.22
50th - 75th	●	0.22 - 0.59
75th - 90th	●	0.59 - 1.8
90th - max	●	1.8 - 14

Median = 0.22 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg

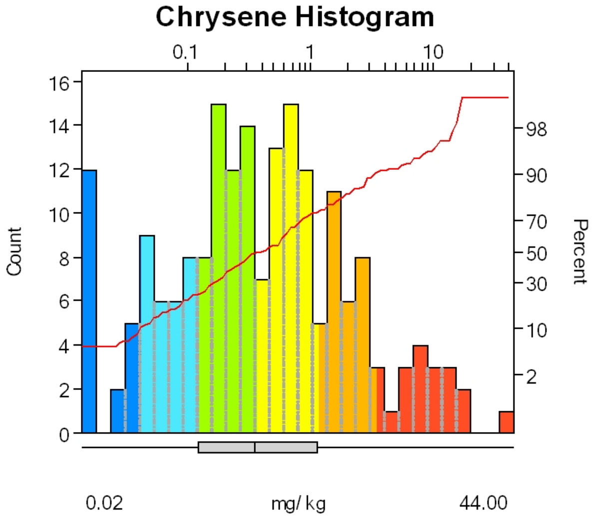




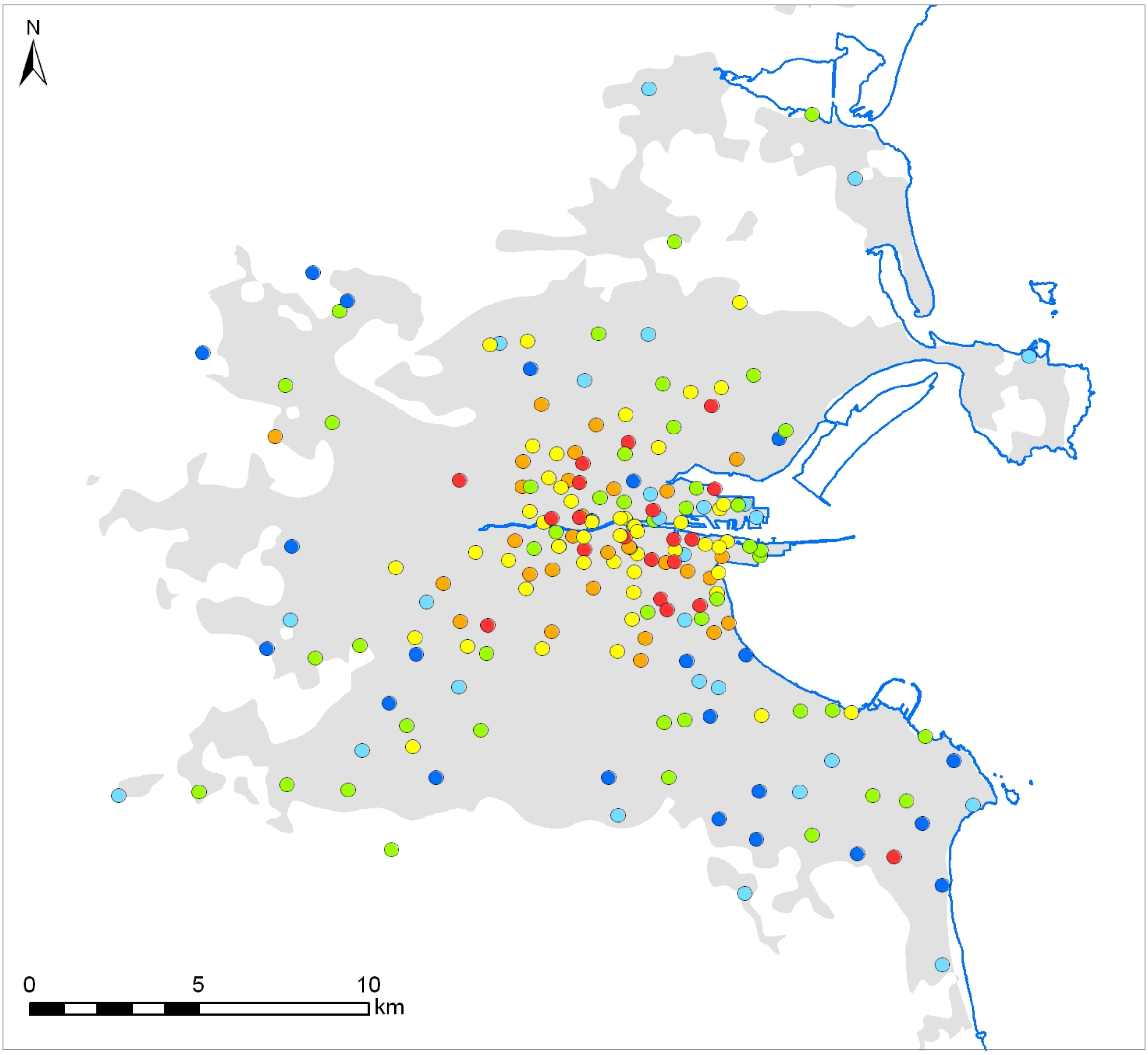
Dublin SURGE Project

Chrysene - topsoil

Percentile		mg/kg
Min - 10th	●	<0.03 - 0.05
10th - 25th	●	0.05 - 0.13
25th - 50th	●	0.13 - 0.37
50th - 75th	●	0.37 - 1.18
75th - 90th	●	1.18 - 3.35
90th - max	●	3.35 - 44



Median = 0.37 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg

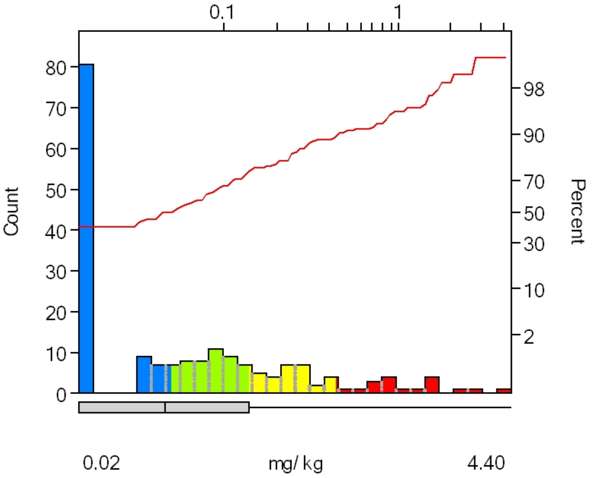


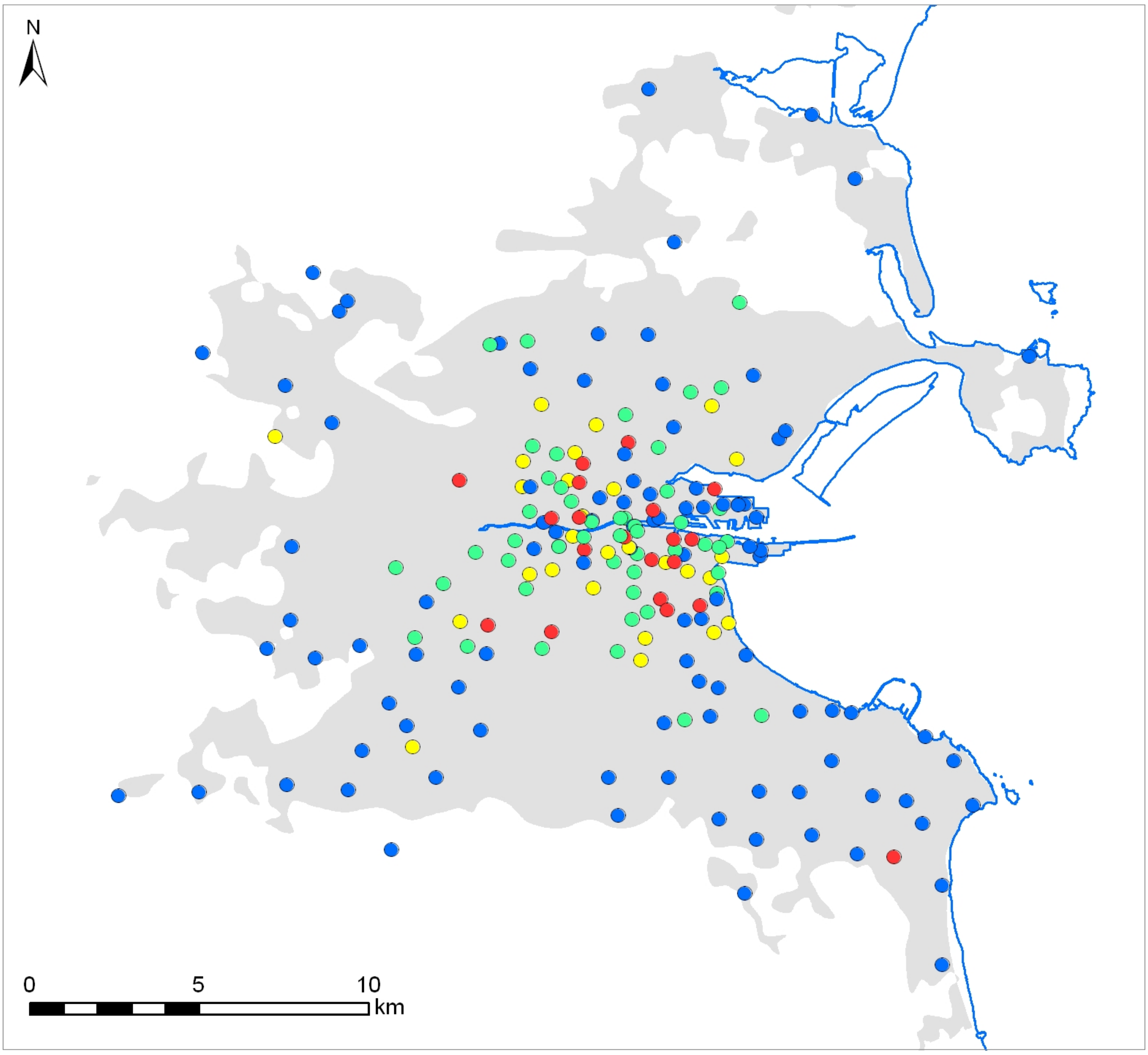
Dublin SURGE Project

Dibenzo(a,h)anthracene - topsoil

Percentile		mg/kg
Min - 50th	●	<0.03 - 0.05
50th - 75th	●	0.05 - 0.14
75th - 90th	●	0.14 - 0.44
90th - max	●	0.44 - 4.4

Median = 0.05 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg


Dibenzo(a,h)anthracene Histogram

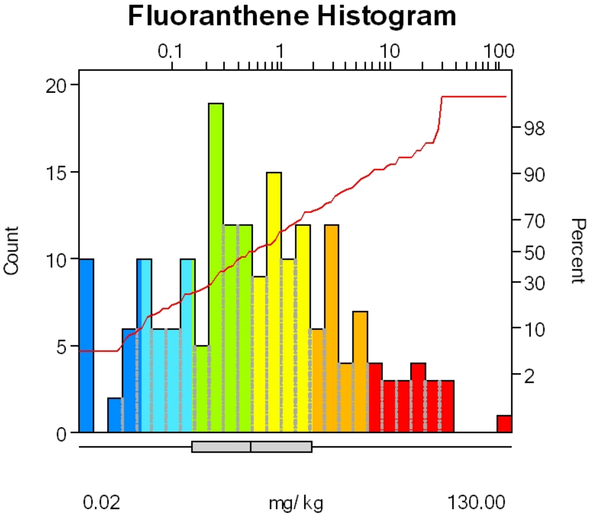


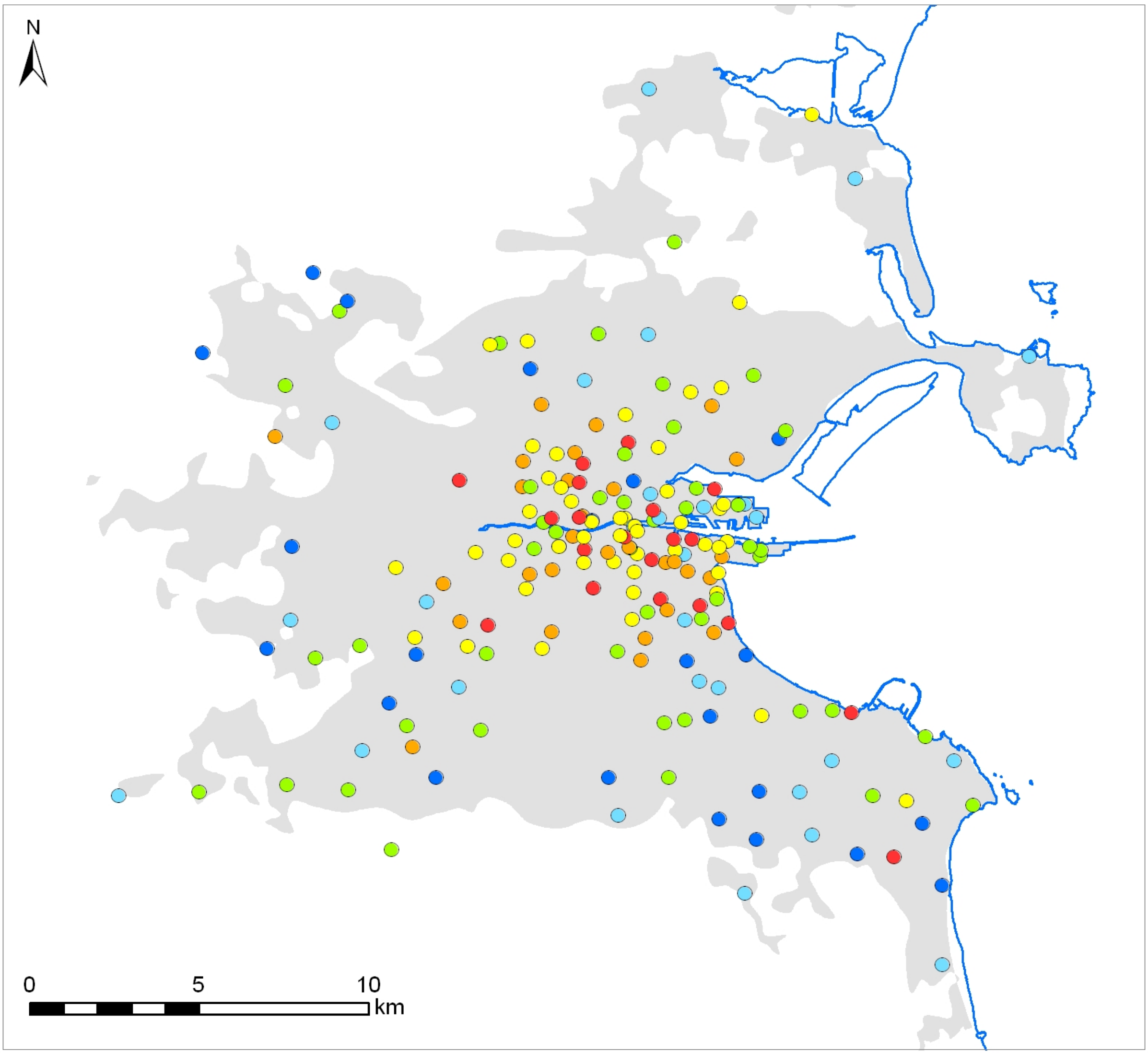
Dublin SURGE Project

Fluoranthene - topsoil

Percentile		mg/kg
Min - 10th	●	<0.03 - 0.06
10th - 25th	●	0.06 - 0.16
25th - 50th	●	0.16 - 0.55
50th - 75th	●	0.55 - 1.98
75th - 90th	●	1.98 - 6.57
90th - max	●	6.57 - 130

Median = 0.55 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg





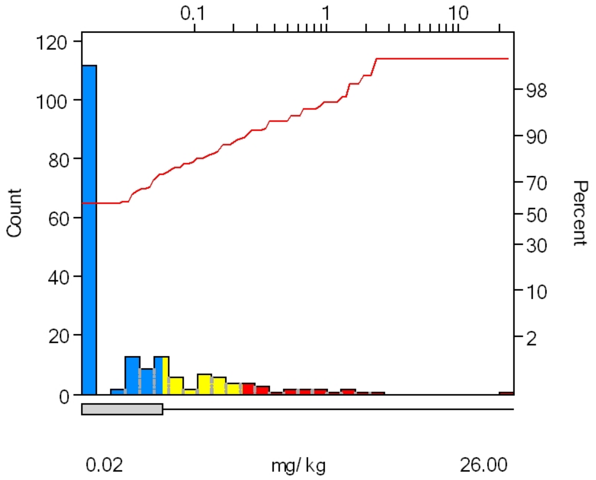
Dublin SURGE Project

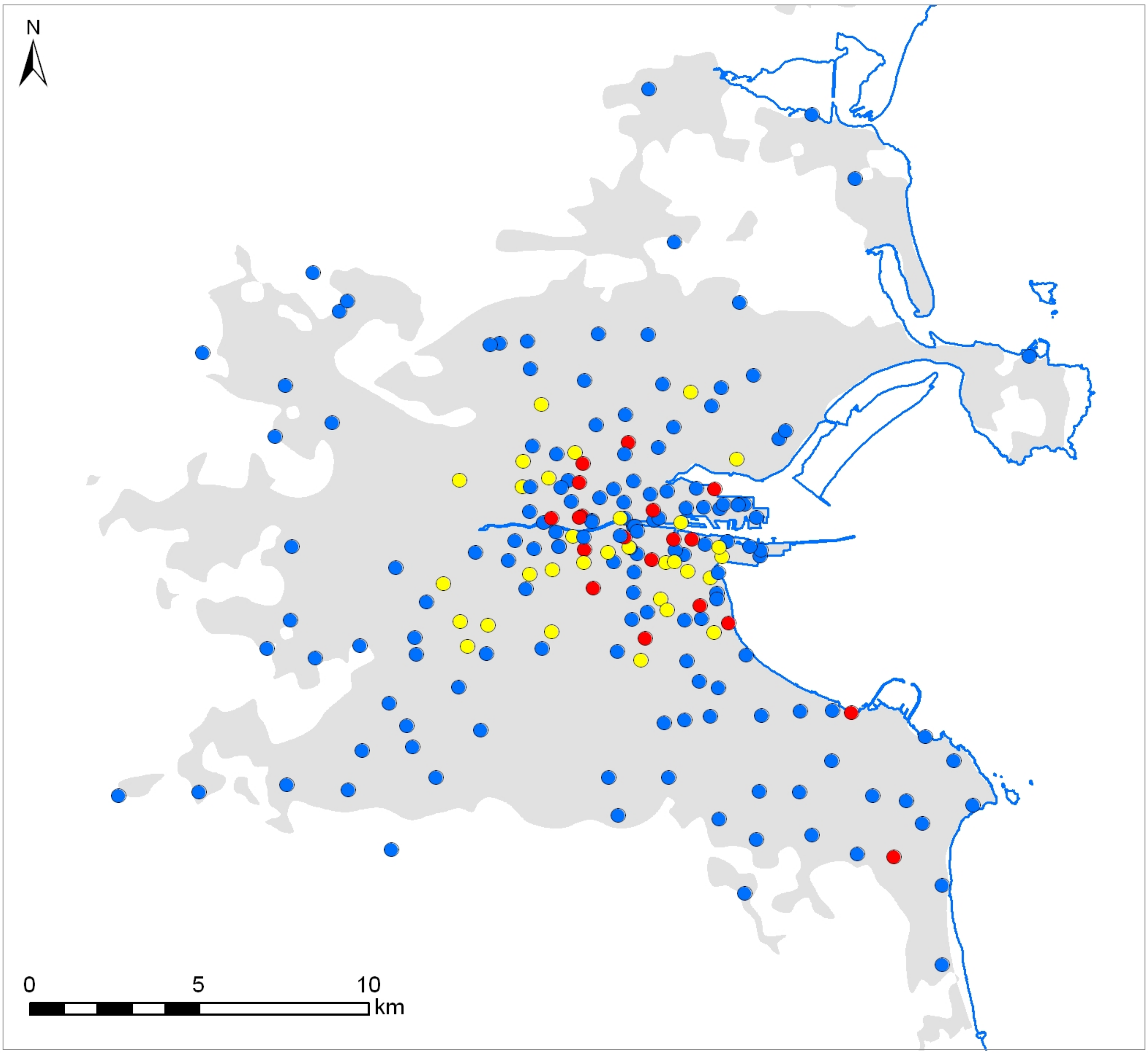
Fluorene - topsoil

Percentile		mg/kg
Min - 75th	●	<0.03 - 0.06
75th - 90th	●	0.06 - 0.24
90th - max	●	0.24 - 26

Median = <0.03 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg

Fluorene Histogram





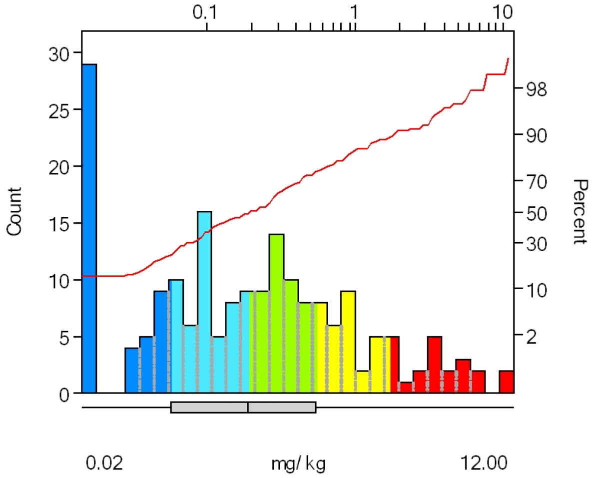
Dublin SURGE Project

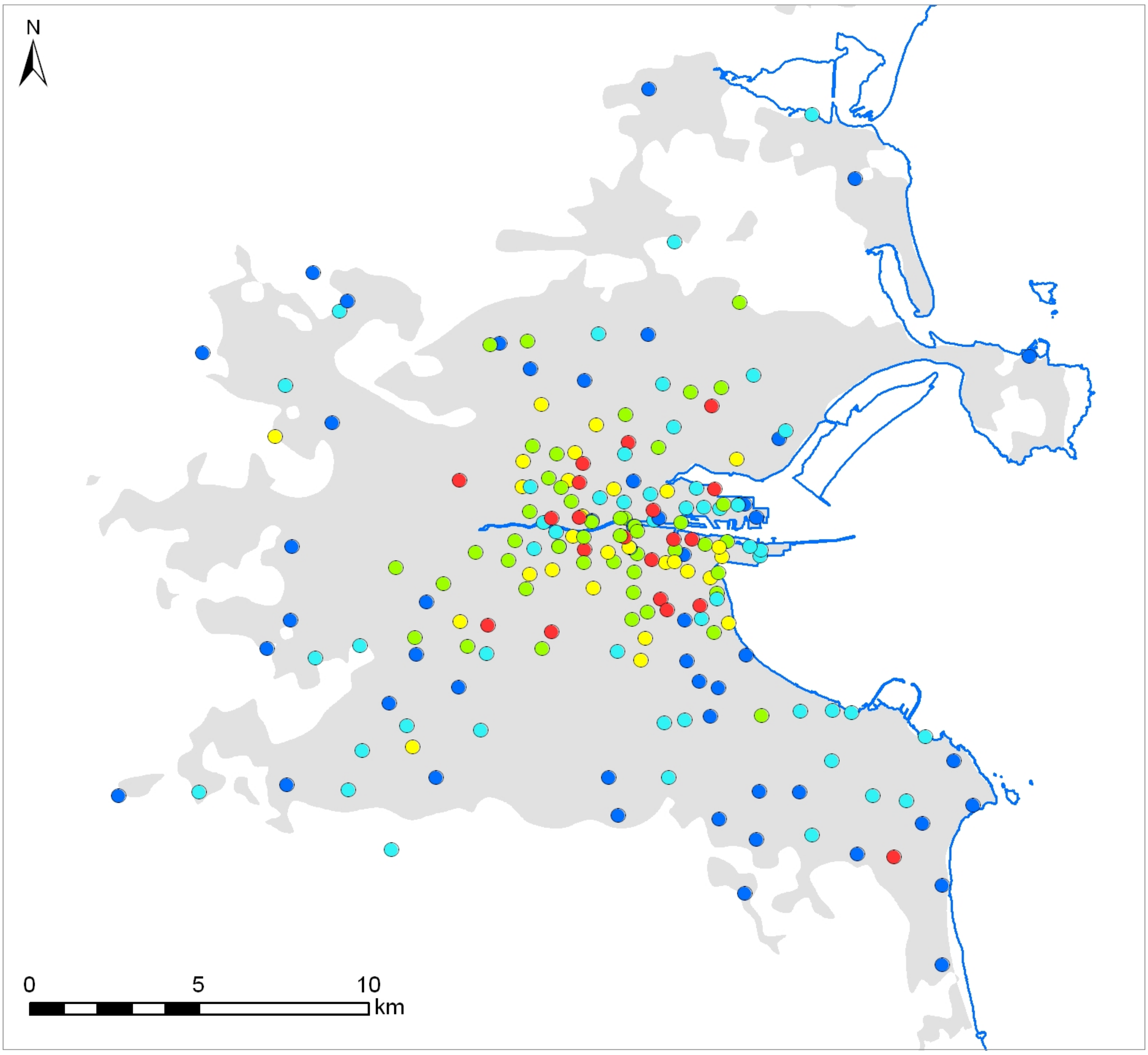
Indeno(1,2,3-c,d)pyrene - topsoil

Percentile		mg/kg
Min - 25th	●	<0.03 - 0.06
25th - 50th	●	0.06 - 0.20
50th - 75th	●	0.20 - 0.57
75th - 90th	●	0.57 - 1.77
90th - max	●	1.77 - 12

Median = 0.20 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg

Indeno(1,2,3-c,d)pyrene Histogram



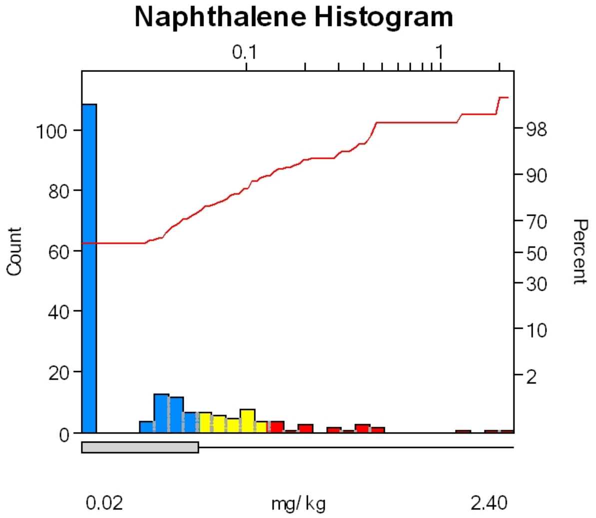


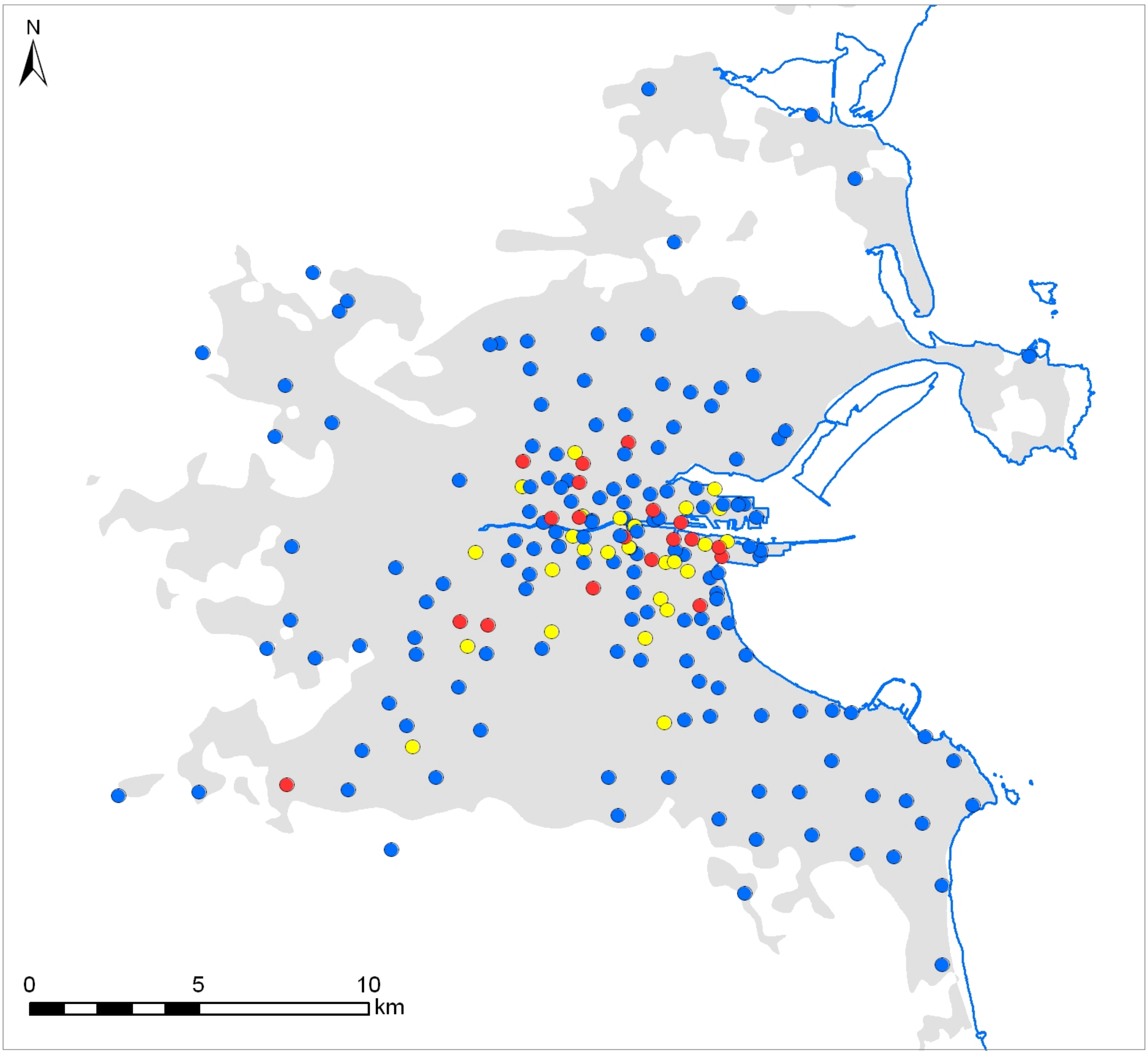
Dublin SURGE Project

Naphthalene - topsoil

Percentile		mg/kg
Min - 75th	🔵	<0.03 - 0.06
75th - 90th	🟡	0.06 - 0.13
90th - max	🔴	0.13 - 2.4

Median = <0.03 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg



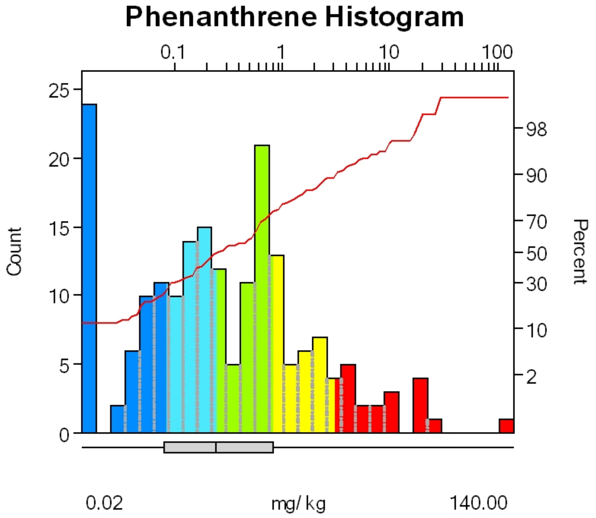


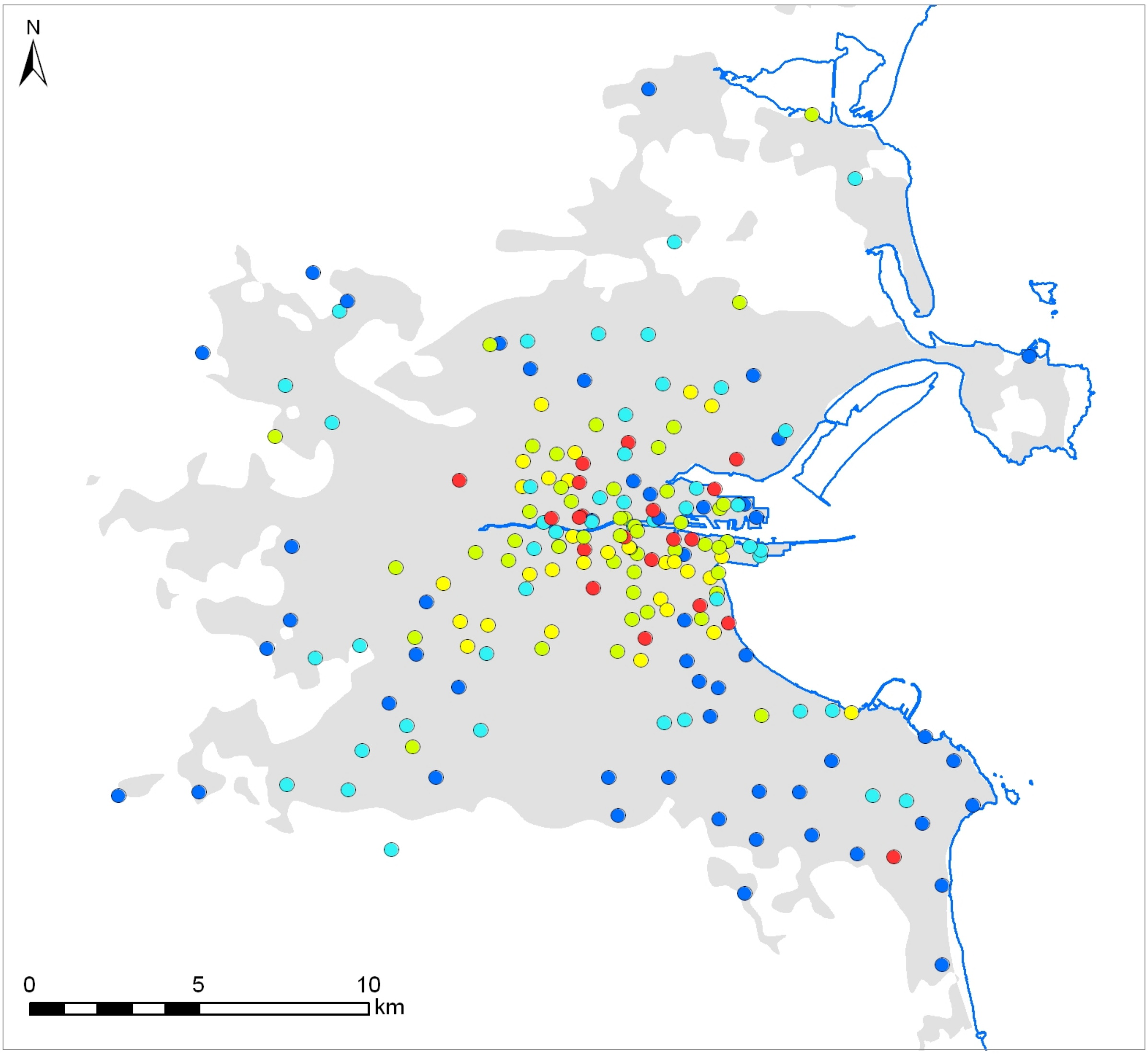
Dublin SURGE Project

Phenanthrene - topsoil

Percentile		mg/kg
Min - 25th	●	<0.03 - 0.09
25th - 50th	●	0.09 - 0.26
50th - 75th	●	0.26 - 0.86
75th - 90th	●	0.86 - 3.14
90th - max	●	3.14 - 140

Median = 0.26 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg


Phenanthrene Histogram



Dublin SURGE Project

Pyrene - topsoil

Percentile		mg/kg
Min - 10th	●	<0.03 - 0.05
10th - 25th	●	0.05 - 0.16
25th - 50th	●	0.16 - 0.53
50th - 75th	●	0.53 - 1.88
75th - 90th	●	1.88 - 5.54
90th - max	●	6.54 - 92

Median = 0.53 mg/kg
Analytical method: GC-MS
Detection limit: 0.03 mg/kg