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Arsenic, heavy metals, PAHs and PCBs in  
surface soils from Dublin, Ireland



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<p>Sammendrag:</p> <p>A systematic survey of the concentration of elements in surface soil in greater Dublin has been carried out in 2009-2010. The soils in central Dublin have high concentrations of lead and polycyclic aromatic hydrocarbons (PAHs). The sampled playgrounds in this survey have high concentrations of lead. Remediation of these playgrounds soils is recommended.</p> <p>The main pollution sources for lead in surface soils are leaded gasoline (a historic source), lead based paints (both a historic and active source), the standing building mass with glazed tiled roofs containing lead (an active source). The main pollution sources for the PAHs are gasworks, energy production, domestic heating, industrial emissions, emission from road traffic and city fires. Urban soils are dynamic because of constant relocation of masses; therefore the spreading of contaminated, excavated masses represents a challenge in the urban environment.</p> <p>The concentration of the other elements and chemical compounds presented in this report are of levels that are safe for human health and show a greater source dependency from natural sources like local bedrock geology than anthropogenic sources.</p>			
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PAH	PCB	Heavy metals	





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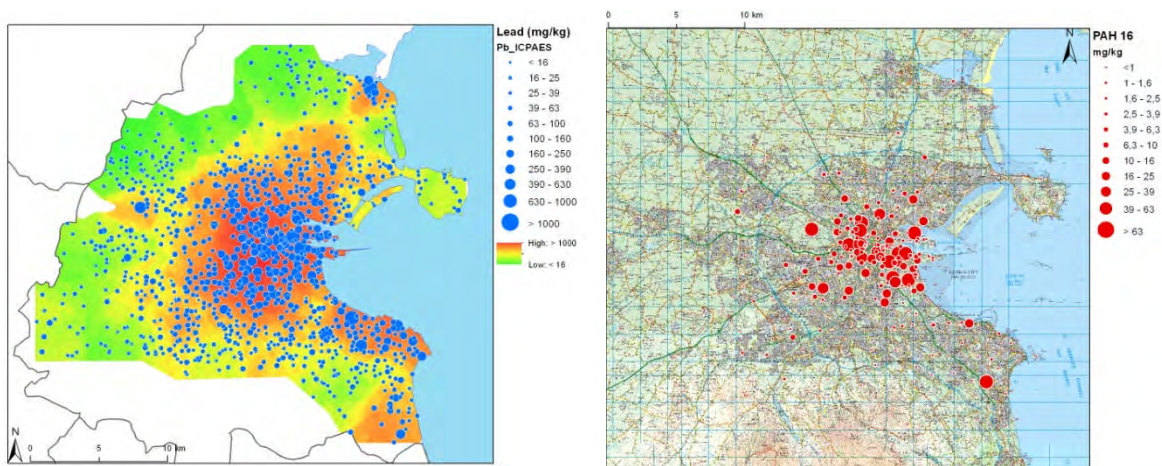
## APPENDIX 1: DETAILED QUALITY CONTROL/ASSESSMENT

## EXECUTIVE SUMMARY

A systematic survey of the concentration of elements in surface soil in greater Dublin has been carried out in 2009-2010. The soils in central Dublin have high concentrations of lead and polycyclic aromatic hydrocarbons (PAHs). The sampled playgrounds in this survey have high concentrations of lead. Remediation of these playgrounds soils is recommended.

The main pollution sources for lead in surface soils are leaded gasoline (a historic source), lead based paints (both a historic and active source), the standing building mass with glazed tiled roofs containing lead (an active source). The main pollution sources for the PAHs are gasworks, energy production, domestic heating, industrial emissions, emission from road traffic and city fires. Urban soils are dynamic because of constant relocation of masses; therefore the spreading of contaminated, excavated masses represents a challenge in the urban environment.

The concentration of the other elements and chemical compounds presented in this report are of levels that are safe for human health and show a greater source dependency from natural sources like local bedrock geology than anthropogenic sources.



Based on the results from this survey a few actions are recommended as follow-up work:

- ✓ Information to the public, local politicians and the Environmental Protection Agency of Ireland (EPA)
- ✓ Lead contamination on all playgrounds should be checked. This can be done very cost effectively using a portable XFR

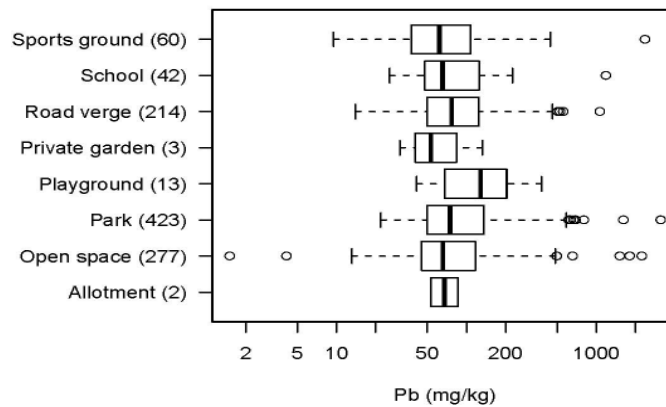
In a longer perspective other actions are recommended:

- ✓ To establish an expert group covering the fields of human health, soil contamination, land use and city planning in order to establish health-based action levels for metals and organic pollutants in Dublin/Irish soils depending on land use.
- ✓ Identify active pollution sources in order to prevent further spreading of contaminants to soils and from land to harbour sediments.

## RECOMMENDATIONS FOR FURTHER USE OF DATA

### Playgrounds

This survey shows that for the heavy metals lead, mercury, copper and zinc, the average concentration is higher in playgrounds than other types of land use areas. The box plots below present the element concentrations for lead in different sampling locations. Lead is known to have serious health effects on humans. The median lead level in surface soil for Dublin playgrounds is 128 mg/kg. The levels for lead in playgrounds are high enough to cause concern.



### Development of 'soil criteria' for land use

In several countries, soil criteria for general types of land use have been established. The soil concentration criteria are developed with human health as the main consideration, taking exposure routes from soil to humans and the duration of exposure into account. This is implemented as a tool for pollution authorities when handling polluted soil and health assessments, an everyday work task within urban building and construction works.

Ireland does not yet have dedicated contaminated land guidance or soil criteria to help landowners assess the potential risks from contaminated land to human health and the environment. By establishing soil criteria in Ireland, the authorities would get a useful tool to easier implement the handling of urban soil and also raise the overall awareness of polluted soil. Soil criteria, guidance and regulations would be established through a collaboration of environmental experts, health authorities and regulators. It is therefore recommended that a contaminated land guidance and regulatory regime is put in place, in order to prevent the deterioration of Ireland's soil resources.

### **Active sources of pollution to harbour sediments**

Active pollution sources within the urban environment can be detected by analysing sediments from storm water culverts within storm water catchment areas in the surface run-off system. Normally, parts of the standing building mass are the important active sources. Urban runoff ends up in the harbour sediments. Contaminated harbour sediments are an environmental challenge. Remediating actions in harbours are not efficient without certain control over the active sources on land.

### **Control of excavating masses**

The results from this survey show elevated levels of several heavy metals in large parts of Dublin. The inner city soil is more polluted by heavy metals than the soil in the outskirts. More awareness on where polluted masses end up during and after excavating work at building sites and roadwork is important in order to minimize the spreading of polluted soil into areas with low levels of pollutants.

## INTRODUCTION

### Background

#### Urban soil

Cities and towns in Europe have been affected by the migration of a large number of people during the last century, largely because of the focus on jobs, goods and services that cities offer. Presently, 80% of the European population lives in cities or towns. The products used in our daily life contribute to pollution of our environment, during their production, use and as waste. Urban soil has been a depository for different sorts of waste during history and it is still an important recipient for pollutants. Typically, urban soil is used and reused several times. Still, a chemical footprint from each generation can be found. Urban geochemical surveys provide an overview on overall chemical composition of urban soils but they also highlight areas for further studies that would address elevated concentrations of potentially harmful elements. Results from soil surveys can be applied within projects concerning land-use planning, human health risk studies, soil contamination and legislation (e.g. Mielke et al. 1983, Abrahams 2002, Fordyce et al. 2005, Ottesen et al. 2008). Some suggestions for further use of the Dublin urban soil survey data are presented further on in the report.

Craul (1985) has modified the urban soil definition of Bockheim (1974), defining urban soil as "soil material having a non-agricultural, man-made surface layer more than 50 cm thick that has been produced by mixing, filling, or by contamination of land surface in urban and suburban areas". He further defined urban soils to have "characteristics unlike those of their natural counterparts" (Craul, 1985).

#### Urban soil surveys

In the third largest city in Norway, Trondheim, the city administration decided in 1994 to undertake a surface soil geochemical baseline mapping study. This geochemical mapping study had a threefold purpose: (1) to assess whether stack emissions from industrial sites, incinerators and crematoria, as well as road traffic, had caused local, traceable pollution, (2) to provide a database for environmental health risk evaluation and (3) to provide background information for further community planning and subsequent soil monitoring studies. This initial urban geochemical study sampled surface soils (0–2 cm) using single samples (Ottesen et al., 1995; Ottesen and Langedal, 2001). This later became the 'Norwegian standard method' for urban geochemical mapping with a sample density of four samples per km<sup>2</sup> (Ottesen et al., 1995; Ottesen and Volden, 1999; Jartun et al., 2002a,b; Andersson et al., 2004).

Different sampling depths have been implemented in urban geochemical surveys world-wide (Ajmone-Marsan and Biasioli, 2010) that differ from the method applied in urban geochemical mapping in Norway (e.g. Ottesen et al., 2008; Andersson et al., 2010). A few other studies have also used the topmost 2 cm, for example in Mexico City (Morton-Bermea et al., 2009), Lubbock, USA (Brown et al., 2008) and Braunschweig, Germany (Wichmann et al., 2007). The 0-25 cm sampling depth has been used in urban geochemical studies for instance in Aubry, France (Douay et al., 2008) and in Damascus, Syria (Möller et al., 2005). In Finland, the sampling depth for urban

topsoil was 0-5 cm in the city of Turku (Salonen and Korkka-Niemi, 2007), 0-15 cm in the city of Pietarsaari (Peltola and Åström, 2003) and 0-40 cm in the city of Helsinki (Salla, 1999). Both the uppermost 25 cm and 2 cm layer of the mineral soil were studied in Tampere Central Region (Jarva et al., 2010).

The main results from urban geochemical studies e.g. in USA and Norway indicate that soils in older parts of the cities are typically contaminated with heavy metals (especially lead, Pb) and polycyclic aromatic hydrocarbons (PAHs). Surface soils in younger suburban parts, that were developed in the 1950s and -60s normally show lower concentrations of metals and PAH. However, polychlorinated biphenyls (PCBs) often occur in these areas. In Norway, where urban soil surveys have been going on since the early 1990s, urban soils are now included in the chemical policy of local and national environmental authorities and the Ministry of the Environment.

### The URGE project

The Geological Surveys of Europe (EuroGeoSurveys) initiated in 2008 a project for studying the chemical content of urban soils in various European cities. A “kick-off meeting” for "Urban Geochemistry in Europe (URGE)" was held in Trondheim in May 2009. It was agreed that the main focus of the project was human health, in order to introduce another angle on urban soil mapping. Therefore, an early/pre-sampling involvement/contact/dialogue with the local health authorities in each city/town was considered a critical success factor. It was agreed upon a sampling depth of 0-10 cm.

Subsequent to the meeting, the Geological Survey of Ireland (GSI) contacted the Geological Survey of Norway (NGU) and asked if NGU could assist in undertaking a geochemical study of the City of Dublin. In August 2009, an agreement on scientific co-operation on mapping of chemical content of hazardous substances in the urban soils of Dublin was signed (Attachment 1).

Late August 2009 a meeting was held in Dublin with participants from the city administration, GSI and NGU. Detailed planning of the project was carried out in September and the fieldwork was completed during two weeks in October 2009. Chemical analyses of the samples were finished in autumn 2010.

### **Urban development of Dublin**

Dublin was founded in 988 A.D. and has grown to a population of approx. 1.219 million (2006), experiencing the most significant growth since the 19<sup>th</sup> century. In historical times Dublin was originally located at the river Liffey near its outlet to Dublin Bay. Since the 1930'ies Dublin has expanded towards the north east and south merging with villages and towns in the outskirts of Dublin, while maintaining the city centre. Horner (1990) has summarized the urban development of Dublin, shown in Figures 1 and 2. Several of these towns and villages have different ages, according to history (Wikipedia, 2010). Some areas date back to pre-Viking – Viking ages like Malahide, Swords, Tallaght, Clondalkin and possibly Naas, which was a walled town in medieval times. Other towns and villages were established in medieval times, including Glasnevin and

Castleknock. Several towns, such as Blackrock, Dun Laoghaire and Palmerstown, were established during the 19<sup>th</sup> century. Walkinstown was established in the 20<sup>th</sup> century. Rathfarnham to the south of Dublin was a local industrial centre, through the establishment of mills and paper production during late 18<sup>th</sup> century.



Figure 1. Maps of Dublin from 1610 (Ireland-information.com) and 1833 (dublinheritage.ie)

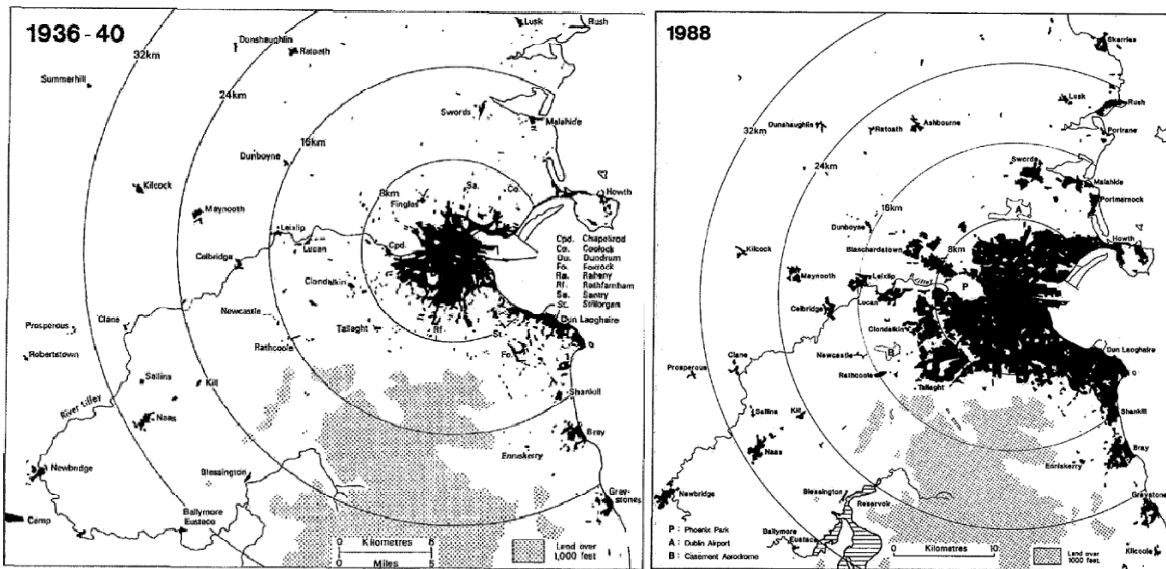


Figure 2. Maps of the growth of Dublin between 1930's and 1980's (Horner, 1990).

The population density (51 inhabitants/km<sup>2</sup> in 1986) in Dublin is markedly lower compared to other European cities, probably due to the combination of a restrictive/conservative high-rise building policy and the availability of land in the outskirts nearby. This might change in years to come as a new development plan is under way (<http://www.dublincitydevelopment plan.ie/>). There are also many open spaces and parks covering large areas throughout the city (Horner, 1990).

Table 1. Urban population in different distance from City center (Horner, 1990)

Distance from city center (km)	1936	1971	1981	1986
0-7 Inner city	266 500	131 500	97 200	83 200
0-7 Rest	211 100	547 100	587 100	546 500
8-15	45 200	140 000	281 000	476 000
16-23	14 700	28 600	52 600	65 300
24- 31	12 500	21 700	39 100	47 800
Total	560 000	868 800	1 050 700	1 218 800

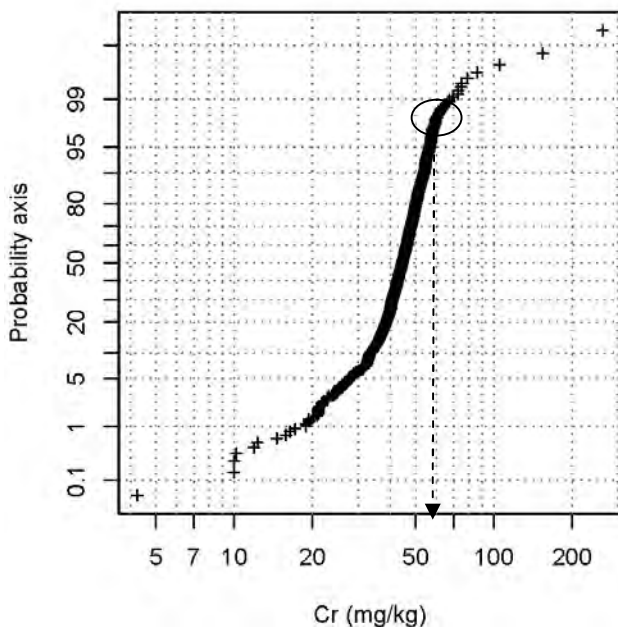


## RESULTS

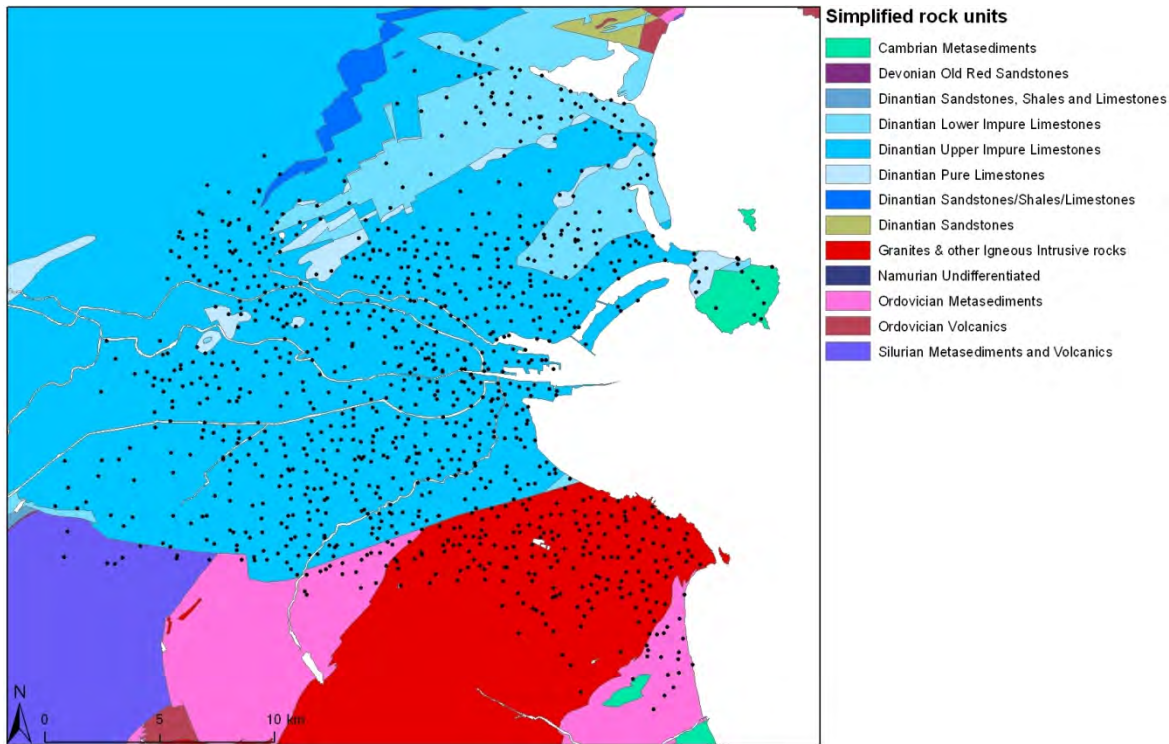
The results for arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc are documented as maps, simple statistics for the whole dataset and in table form for 18 city districts, which are shown in Figure 5.

The natural background level for surface soil is provided for each element. This has been extracted as a visual assessment from the cumulative frequency distribution, which is provided on the map page for each element. The natural background level can be defined as the statistical value of the concentration for an element, which is a result of natural geological and pedological processes excluding anthropogenic input (Dominguez, 2008). The background level is occasionally presented as a concentration range since urban soil is very heterogeneous and the value can vary considerably over short distances.

The cumulative frequency distribution presents the distribution of an element in one curve (Figure 3) which in most instances presents more than one population, or source in this context. A break in the curve indicates a division between two element sources (Bølviken, 1973). When a sufficient number of results are present, a break in the curve is considered the division between the natural and the anthropogenic contribution. The concentration at the break will indicate the natural, upper level for the element. The estimate of natural values of Dublin soil are supported by the results of eight samples from the National Soil Databank from the outskirts of Greater Dublin Area that were inserted in this analytical series. These results are referred to as NSD-values in the following text.



**Figure 3. Cumulative frequency distribution where a break in the curve is indicated, presenting the upper limit of the natural level of the element.**



**Figure 4. Simplified geological map with sample sites marked (GSI, 2010).**

The bedrock geology of Dublin city and surrounding areas is shown in Figure 4. Dublin city is underlain by the Dublin Basin, a geological region composed of poorly differentiated Lower Carboniferous basinal limestones and shale, known 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 and shale 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, which consists of peraluminous granites (those in which the proportion of aluminium oxide is greater than the total alkali oxides) (McConnell, 1994). The Leinster granite batholith is surrounded by a metamorphosed region of fine grained metasediments (schists, shales and siltstones) (McConnell, 1994). Most mineralisation in the study area is associated with the margins of the Leinster batholith in the south Co. Dublin. Economic minerals mined in this area include 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 20m) and areas of thick alluvial material along the River Liffey (Naylor, 1995). Subsoil composition is dominated by the parent lithology, with tills mainly derived from black shale interbedded limestone in central and northern Dublin city, and tills derived from granites in the south.

## Map production and statistics

The geochemical maps were made in ArcGIS 9.3 (ESRI). Kriging maps were produced by Geochemistry for ArcGIS by GeoSoft Inc. For kriging, a cell size of 100 was chosen for all contour maps. The nugget effect was typically close to zero (0 - 0.03), sill ranged from 0.0075 - 0.066 and the range was typically 1000 (300-1000). A contour border was set by hand. Growing dot symbology were carefully chosen by an evaluation of the cumulative frequency distribution for each element in relation to a five division of the logarithmic scale (Bølviken, 1973) and symbols with exponentially growing dot size.

Basic statistics were calculated for each element with regards to the 18 city/Garda districts (Figure 5) that the sampling covered. These areas were chosen as they are subsets of the six Dublin metropolitan regions (DMR), and represent suitably small areas to tell local differences in concentrations, but large enough to provide sound statistical results.

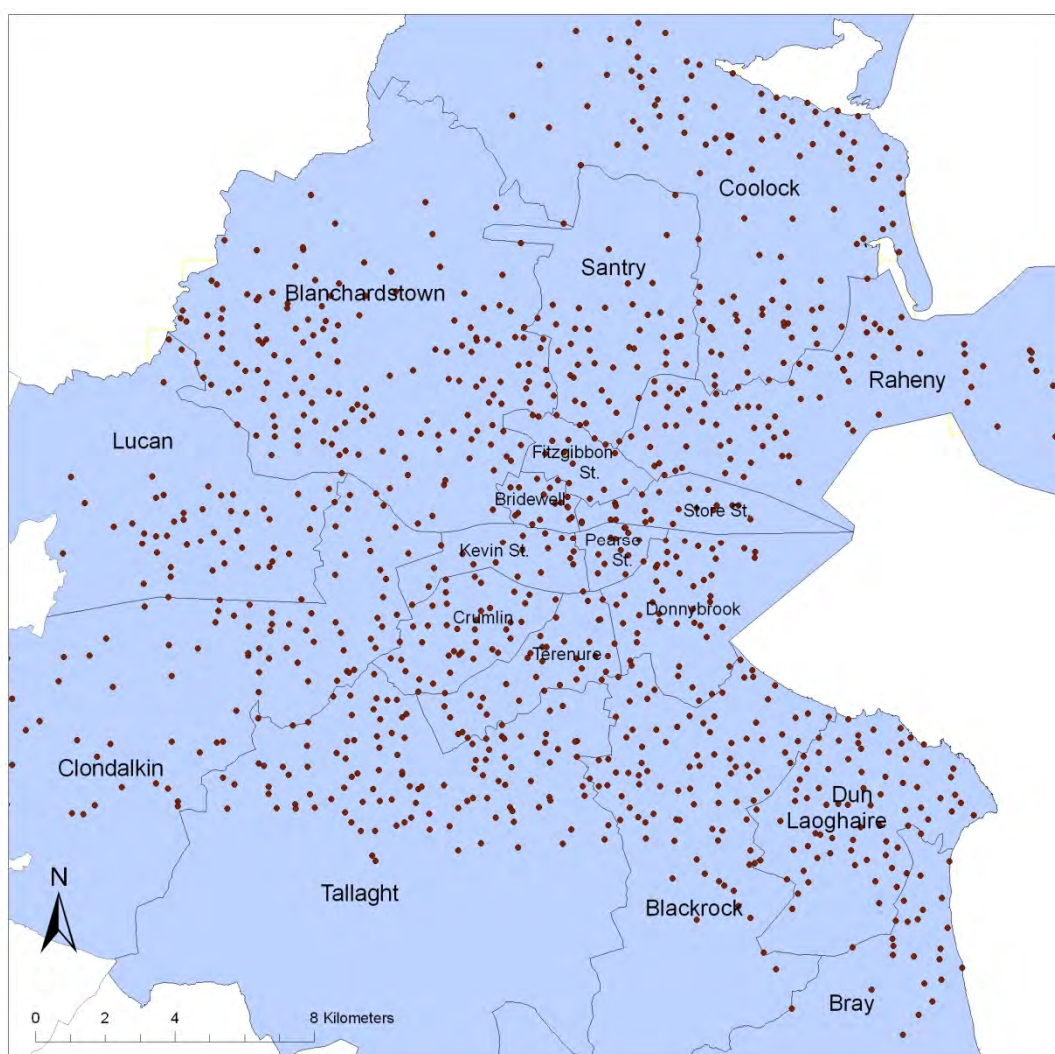
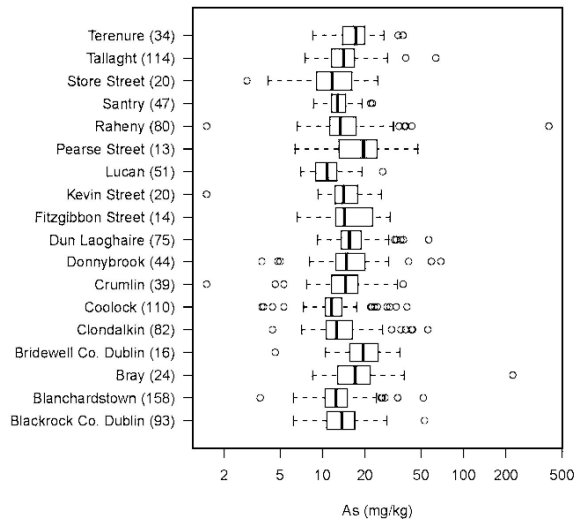
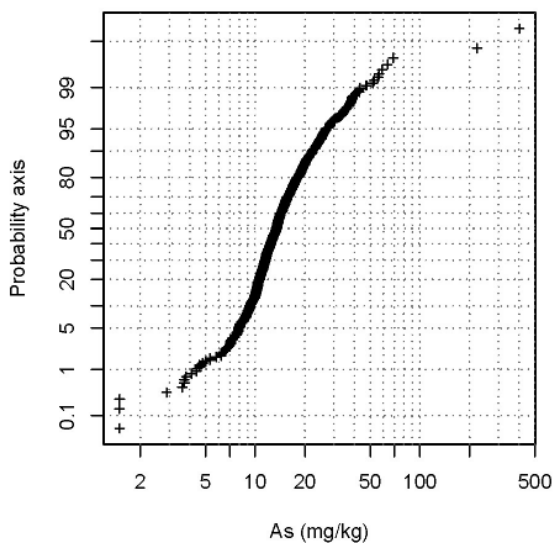
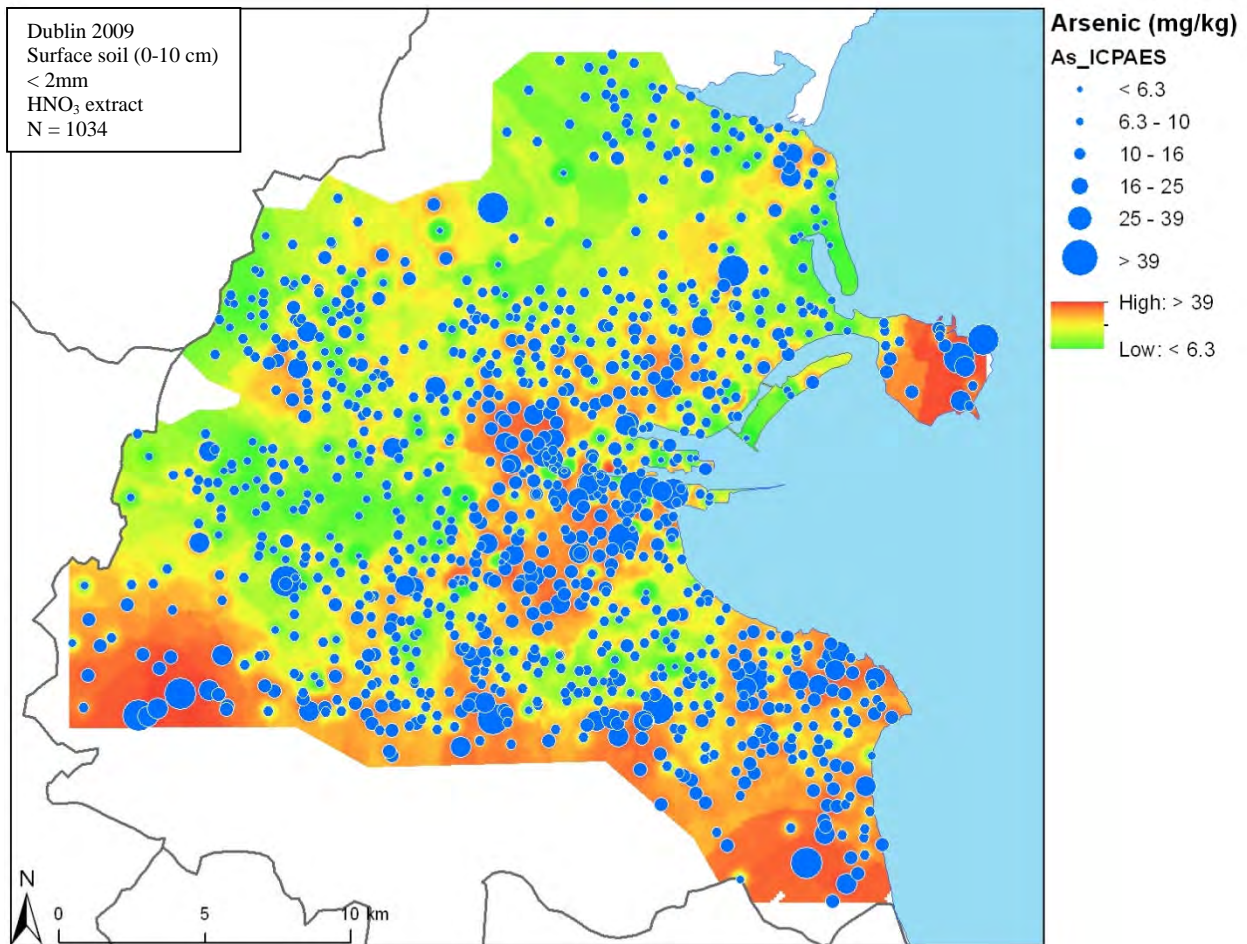


Figure 5. The 18 city districts used in basic statistics within this report with sampling locations.





## Arsenic (As)

### Sources (Anthropogenic and natural)

Arsenic is being used in wood preservatives, alloys, ammunition, semi-conductors, batteries, paints, textiles and tanning. Anthropogenic sources also includes industrial processes and domestic heating using coal (Reimann and Caritat 1998). Arsenic mainly occurs as arsenic inorganic salts, and is mainly contaminating soil in an urban setting through the leaching of impregnated wood and the burning of fossil fuel.

The Dublin area presents higher arsenic levels than in other parts of Ireland due to the local geology (Fay et al. 2007).

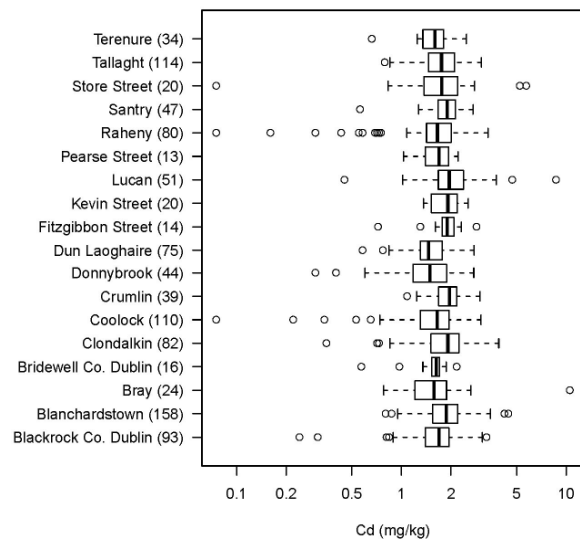
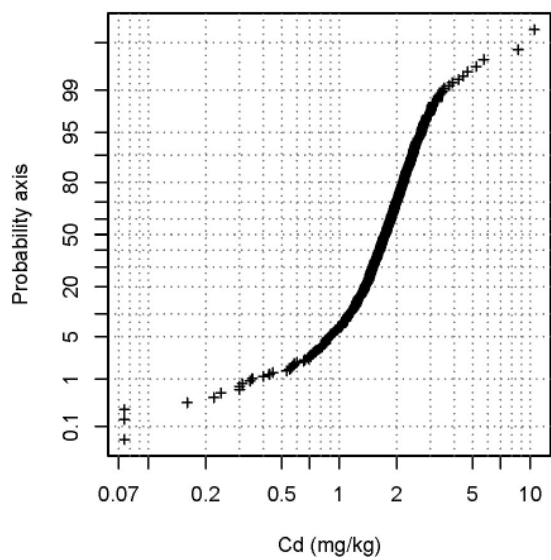
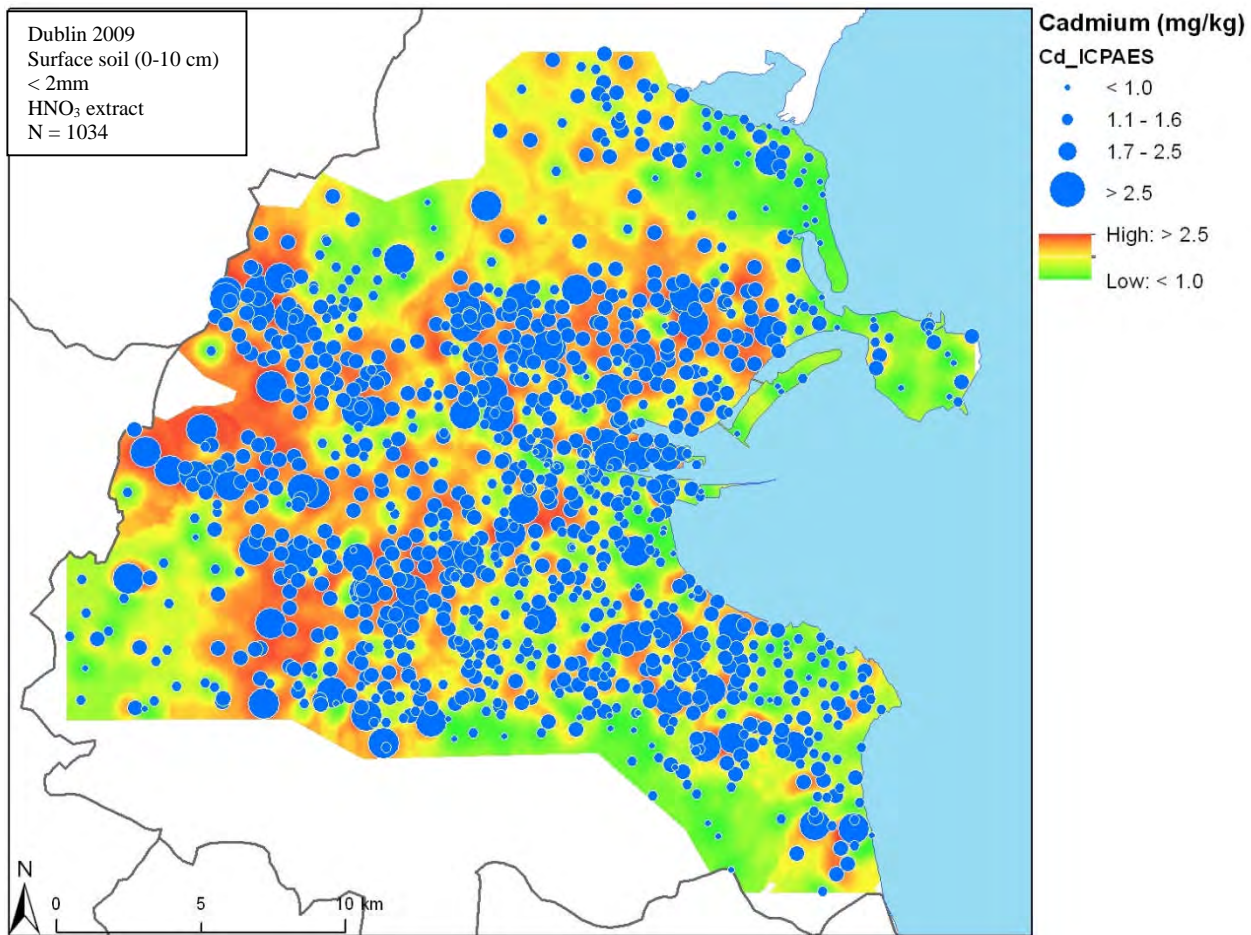
### Health

High doses of arsenic are acutely toxic or may give symptoms in the intestines. Chronic arsenic exposure can result in skin cancer through dermal contact and lung cancer by inhalation over time. In general, the main source of arsenic for humans is food, fish and seafood being the main contributor. Organic arsenic from marine environments is not considered detrimental to health.

### Results

The distribution of arsenic indicates both a geological and anthropogenic sources for this element. Higher levels of arsenic occur in the areas of metasediments and volcanics in the south and on Howth. In addition, the anthropogenic factor can be seen in the central parts of Dublin. Based on the cumulative distribution curve, two arsenic populations can be identified (natural and anthropogenic). The natural level of arsenic in Dublin surface soils varies between 1 to 20 mg/kg, NSD-values 10 – 27 mg/kg.

DMR	Garda	N (number of samples)	Min	Median	Mean	Max
<b>Whole area</b>		<b>1034</b>	<b>1.5</b>	<b>13</b>	<b>16</b>	<b>402</b>
Northern	Coolock	110	3.7	12	13	40
	Raheny	80	1.5	13	20	402
	Santry	47	8.6	13	14	23
Western	Blanchardstown	158	3.6	12	14	52
	Clondalkin	82	4.4	13	15	56
	Lucan	51	7.0	11	11	27
North Central	Bridewell	16	4.6	20	20	35
	Fitzgibbon Street	14	6.6	14	17	30
	Store Street	20	2.9	12	13	25
South Central	Donnybrook	44	3.7	15	18	69
	Pearse Street	13	6.4	20	20	47
	Kevin Street	20	1.5	14	15	26
Southern	Crumlin	39	1.5	15	15	37
	Tallaght	114	7.5	14	15	64
	Terenure	34	8.5	17	18	37
Eastern	Blackrock	93	6.2	14	15	53
	Bray	24	8.5	17	27	223
	Dun Laoghaire	75	9.2	16	18	57



## Cadmium (Cd)

### Sources (Anthropogenic and natural)

Cadmium is being used in electroplating, Ni-Cd batteries, pigments, stabilisers for plastics, soldering and very low melting point alloys. Anthropogenic sources include coal combustion, smelters, iron and steel mills, electroplating, fertilisers, traffic, sewage sludge, waste water and waste incineration (Reimann and Caritat, 1998). Cadmium is normally associated with zinc in natural soils.

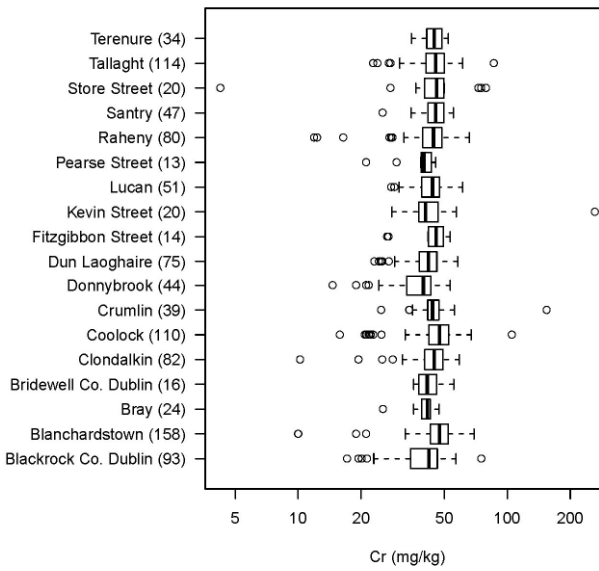
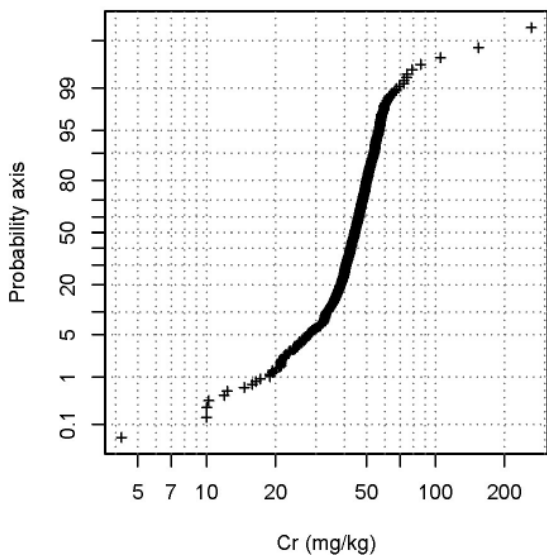
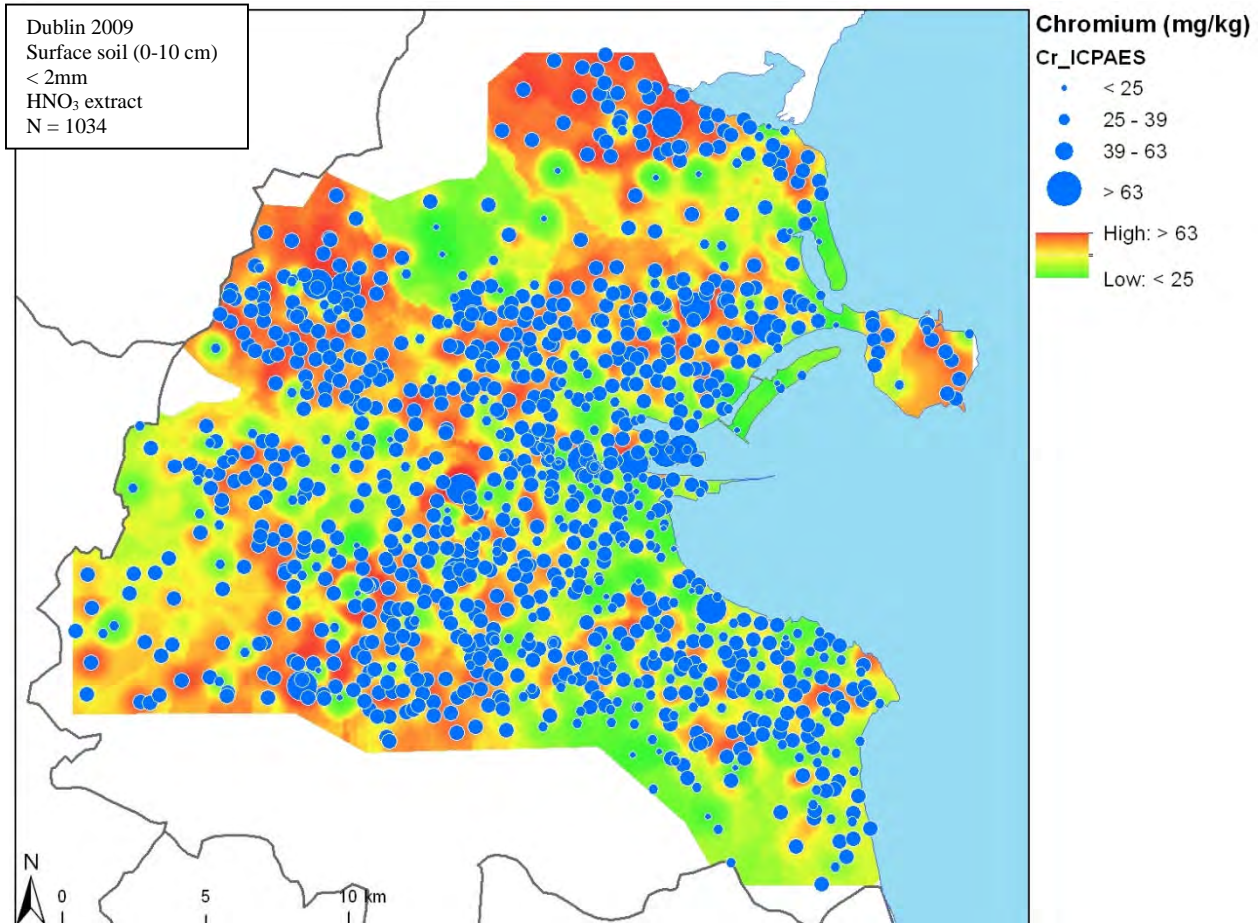
### Health

Cadmium is for humans a non-essential metal. It is detrimental for the health as it is accumulated in the body, especially in the kidneys. Therefore long term exposure to cadmium is increasingly damaging. Cadmium may cause cancer and damage the calcium metabolism, thereby damaging the bones. In general, there are low levels of cadmium in food. Tobacco is the most significant source for smokers, since cadmium is taken up more efficiently from the lungs.

### Results

Naturally high levels of cadmium in the Dublin area are due to the underlying impure limestone (Fay et al., 2007). The cadmium level is considerably higher compared to Norwegian cities where the median level for cadmium is between 0.2 - 0.3 mg/kg. Based on the cumulative frequency distribution two cadmium populations are identified (natural and anthropogenic). The natural level of cadmium in Dublin surface soils varies between 0.08 – 3 mg/kg, NSD-values 0.6 – 2.1 mg/kg.

DMR	Garda	N	Min	Median	Mean	Max
Whole area		1034	0.08	1.7	1.8	11
Northern	Coolock	110	0.08	1.7	1.6	3.0
	Raheny	80	0.08	1.7	1.6	3.4
	Santry	47	0.56	1.9	1.9	2.7
Western	Blanchardstown	158	0.80	1.9	1.9	4.5
	Clondalkin	82	0.35	1.9	1.9	3.9
	Lucan	51	0.45	2.0	2.2	8.7
North Central	Bridewell	16	0.57	1.6	1.6	2.2
	Fitzgibbon Street	14	0.72	1.9	1.9	2.9
	Store Street	20	0.08	1.8	2.0	5.7
South Central	Donnybrook	44	0.30	1.5	1.5	2.8
	Pearse Street	13	1.0	1.7	1.7	2.2
	Kevin Street	20	1.4	1.9	1.9	2.5
Southern	Crumlin	39	1.1	2.0	2.0	3.0
	Tallaght	114	0.79	1.8	1.8	3.1
	Terenure	34	0.66	1.6	1.6	2.5
Eastern	Blackrock	93	0.24	1.7	1.7	3.3
	Bray	24	0.78	1.6	1.9	11
	Dun Laoghaire	75	0.58	1.5	1.6	2.8





## Chromium (Cr)

### Sources (Anthropogenic and natural)

Chromium is being used in stainless steel, many other alloys, chrome plating, pigments, catalysts, dye, tanning, wood impregnation, refractory bricks and magnetic tapes. Anthropogenic sources therefore include chemical industry, steel works, electrometallurgy, copper smelting, combustion of natural gas, oil and coal, sewage sludge, waste incineration and some phosphorus fertilizers (Reimann and Caritat, 1998). Mafic and ultramafic rocks are natural sources for chromium.

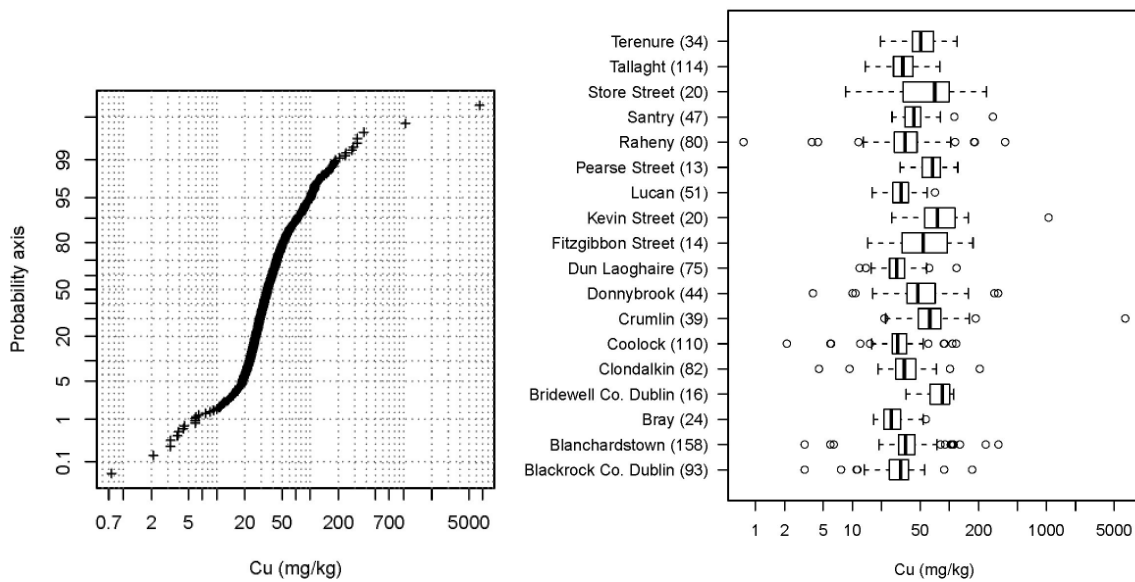
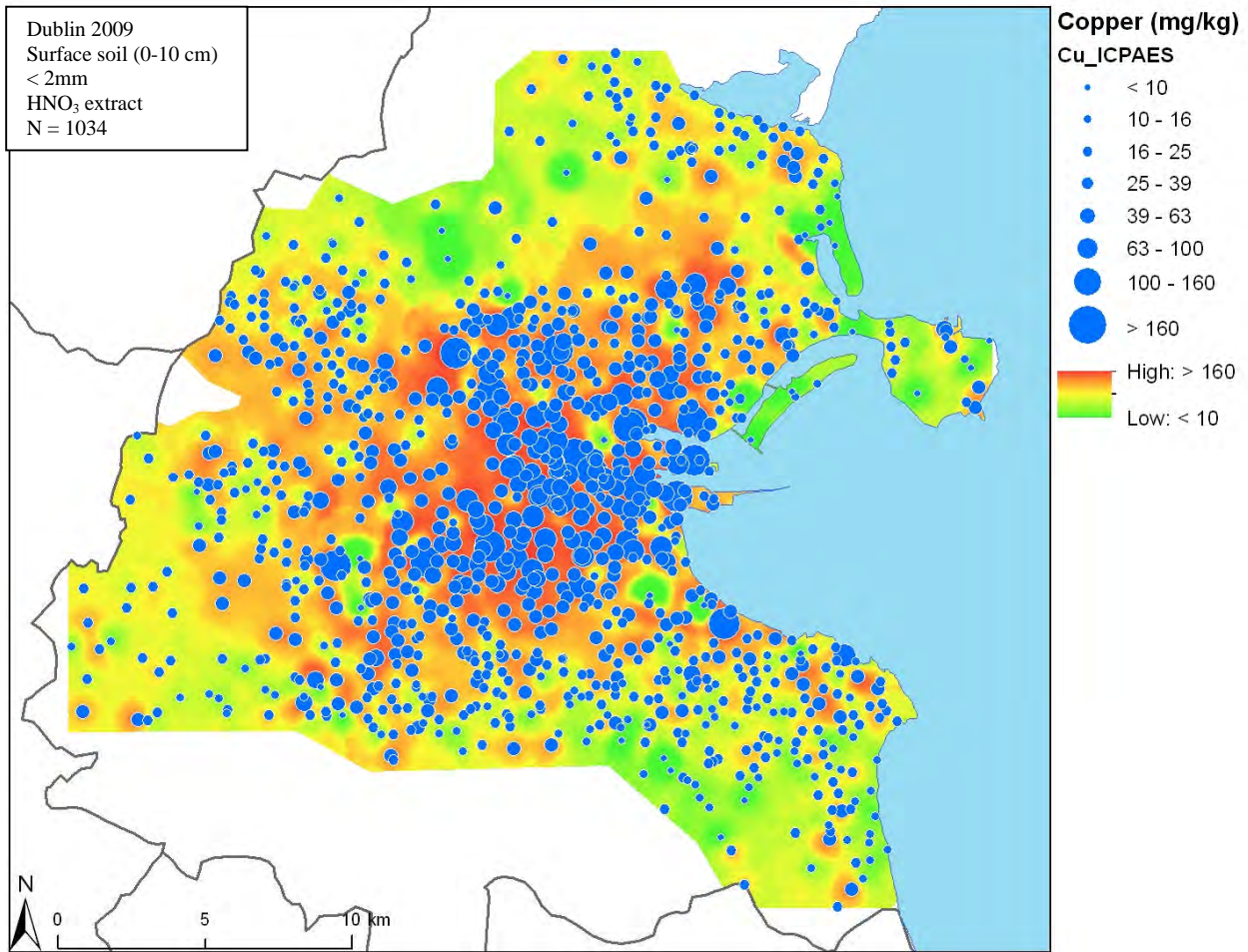
### Health

Chromium occurs in two main forms; Cr(III) and Cr(VI). Cr(III) is essential for humans and does not pose a health risk, in contrast to the more easily soluble, but instable Cr(VI), which is highly toxic. The main sources of chromium are from food made in stainless steel cooking pots as well as tobacco for smokers. Cr(VI), which is mainly produced in industrial processes is easily taken up in humans, causing allergies by dermal contact and cancer by inhalation. The combination of high levels of zinc, cadmium, lead or arsenic and chromium can be an indicator of Cr(VI) (Rose et al., 1979). If the correlation factor between chromium and nickel is very high, it indicates that the main source of chromium is geogenic. This reduces the possibility to detect Cr(VI) (Goldschmidt, 1954). In other words, a high ratio between chromium and nickel should be considered a signal of non-geogenic chromium.

### Results

In the Dublin area, the levels of chromium are generally reasonably low due to low levels in the underlying limestone. Most of the chromium has natural sources and only about 2 % of the samples are contaminated as can be seen from the cumulative frequency distribution. The natural chromium value varies between 4 and 60 mg/kg, NSD-values 21 – 59 mg/kg.

DMR	Garda	N	Min	Median	Mean	Max
Whole area		1034	4.2	44	44	262
Northern	Coolock	110	16	47	46	105
	Raheny	80	12	44	43	66
	Santry	47	25	45	45	55
Western	Blanchardstown	158	10	47	47	69
	Clondalkin	82	10	45	44	59
	Lucan	51	28	44	43	61
North Central	Bridewell	16	36	42	43	56
	Fitzgibbon Street	14	27	46	44	53
	Store Street	20	4.2	46	48	79
South Central	Donnybrook	44	15	40	38	53
	Pearse Street	13	21	40	39	46
	Kevin Street	20	28	41	53	262
Southern	Crumlin	39	25	44	47	154
	Tallaght	114	23	46	45	86
	Terenure	34	35	45	45	52
Eastern	Blackrock	93	17	42	41	75
	Bray	24	25	42	41	47
	Dun Laoghaire	75	23	42	41	58



## Copper (Cu)

### Sources

Copper is being used in electrical industry, water piping, pigments, alloys, coins, algacides, bactericides, molluscicides, fungicides and insecticides. Anthropogenic sources therefore include copper mining and smelting, electrical industry, agriculture, sewage sludge and steel works (Reimann and Caritat, 1998). Mafic and ultramafic rocks are natural sources for copper.

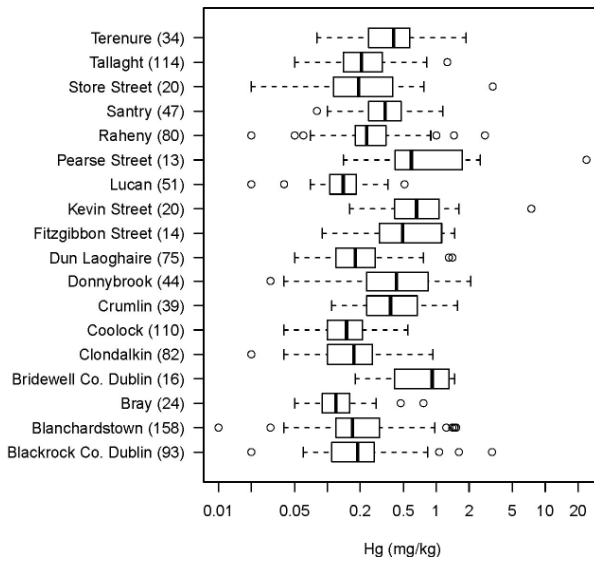
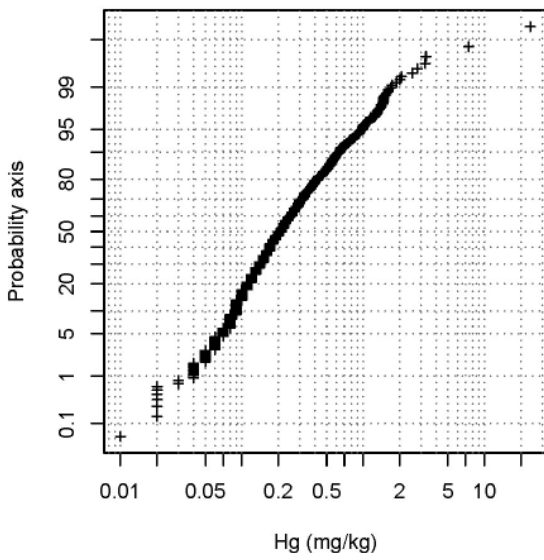
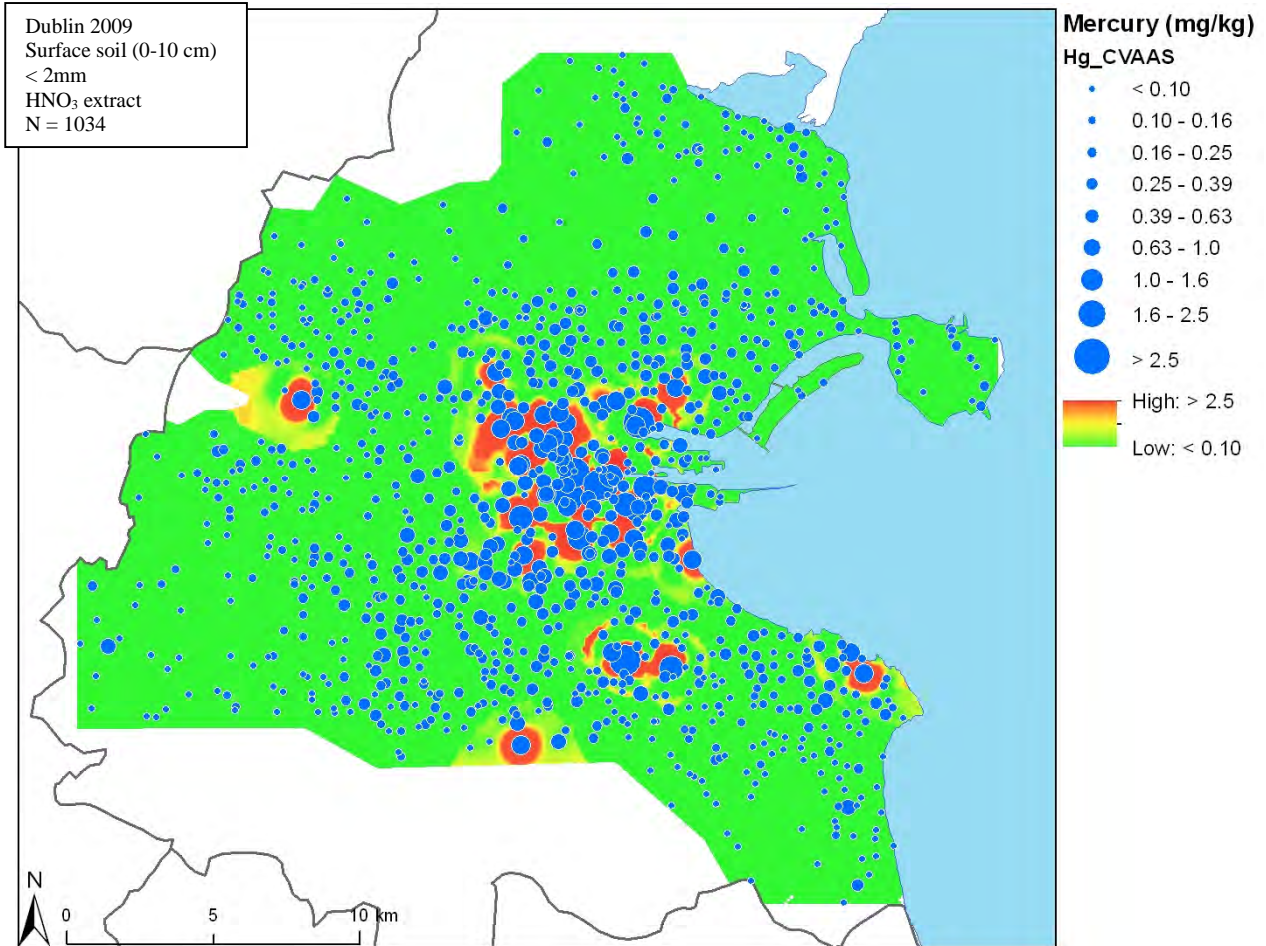
### Health

Copper is an element that is essential for humans. The main source of copper is from food. Only very high levels of copper in soil pose a risk to human health.

### Results

Copper presents higher levels towards the central parts of Dublin, which seems to indicate an anthropogenic contribution. Generally in Ireland, the areas with greywackes including volcanics have elevated levels of copper. The natural copper content in surface soils in Dublin varies between < 1 to 50 mg/kg, NSD-values 13 – 52 mg/kg.

DMR	Garda	N	Min	Median	Mean	Max
<b>Whole area</b>		<b>1034</b>	<b>0.75</b>	<b>35</b>	<b>51</b>	<b>6480</b>
Northern	Coolock	110	2.1	29	33	117
	Raheny	80	0.75	35	46	374
	Santry	47	26	43	49	280
Western	Blanchardstown	158	3.2	35	43	319
	Clondalkin	82	4.5	34	39	205
	Lucan	51	16	32	34	71
North Central	Bridewell	16	36	85	83	111
	Fitzgibbon Street	14	14	54	66	175
	Store Street	20	8.5	71	77	241
South Central	Donnybrook	44	3.9	47	66	317
	Pearse Street	13	31	67	67	122
	Kevin Street	20	26	75	128	1050
Southern	Crumlin	39	21	63	232	6480
	Tallaght	114	14	33	35	80
	Terenure	34	20	51	56	120
Eastern	Blackrock	93	3.2	31	33	171
	Bray	24	17	25	28	57
	Dun Laoghaire	75	12	29	31	118



## Mercury (Hg)

### Sources

Mercury is being used in the production of caustic soda and chlorine, gold ore processing, batteries, dentistry, wood impregnation, thermometers, barometers, detonators, fungicide in mercury staining of seed grains and Hg-vapor lamps. Environmental pathways are windblown dust, sea spray and volcanic dust. Anthropogenic sources include open cast mining (detonators), crude oil and coal combustion (Hg is present in sulphide mineral impurities), chemical industry, electric lamp production, paper mills and sewage sludge (Reimann and Caritat, 1998).

### Health

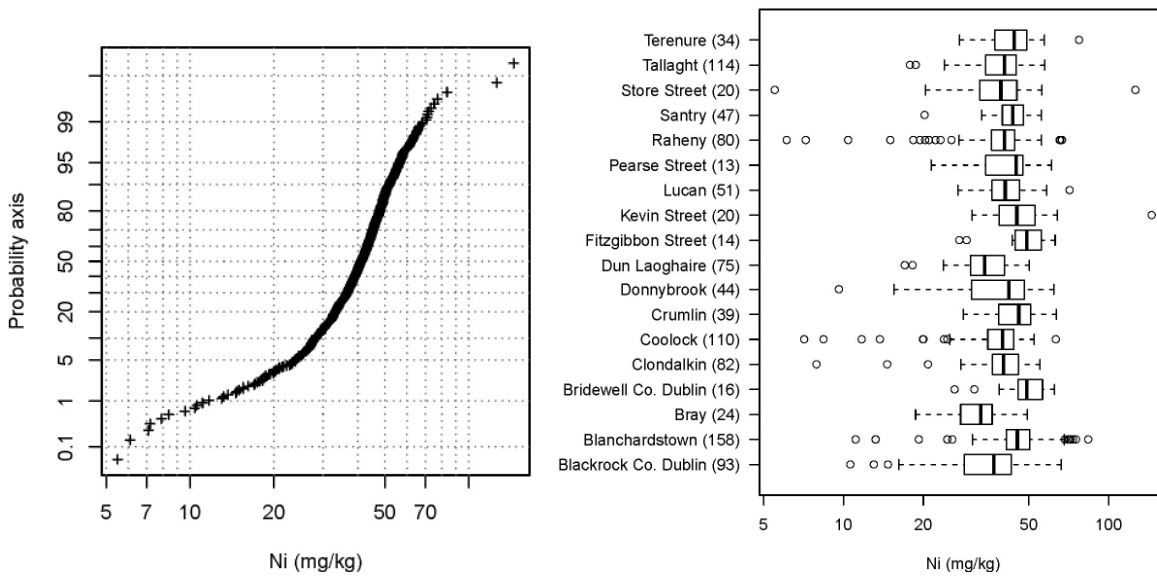
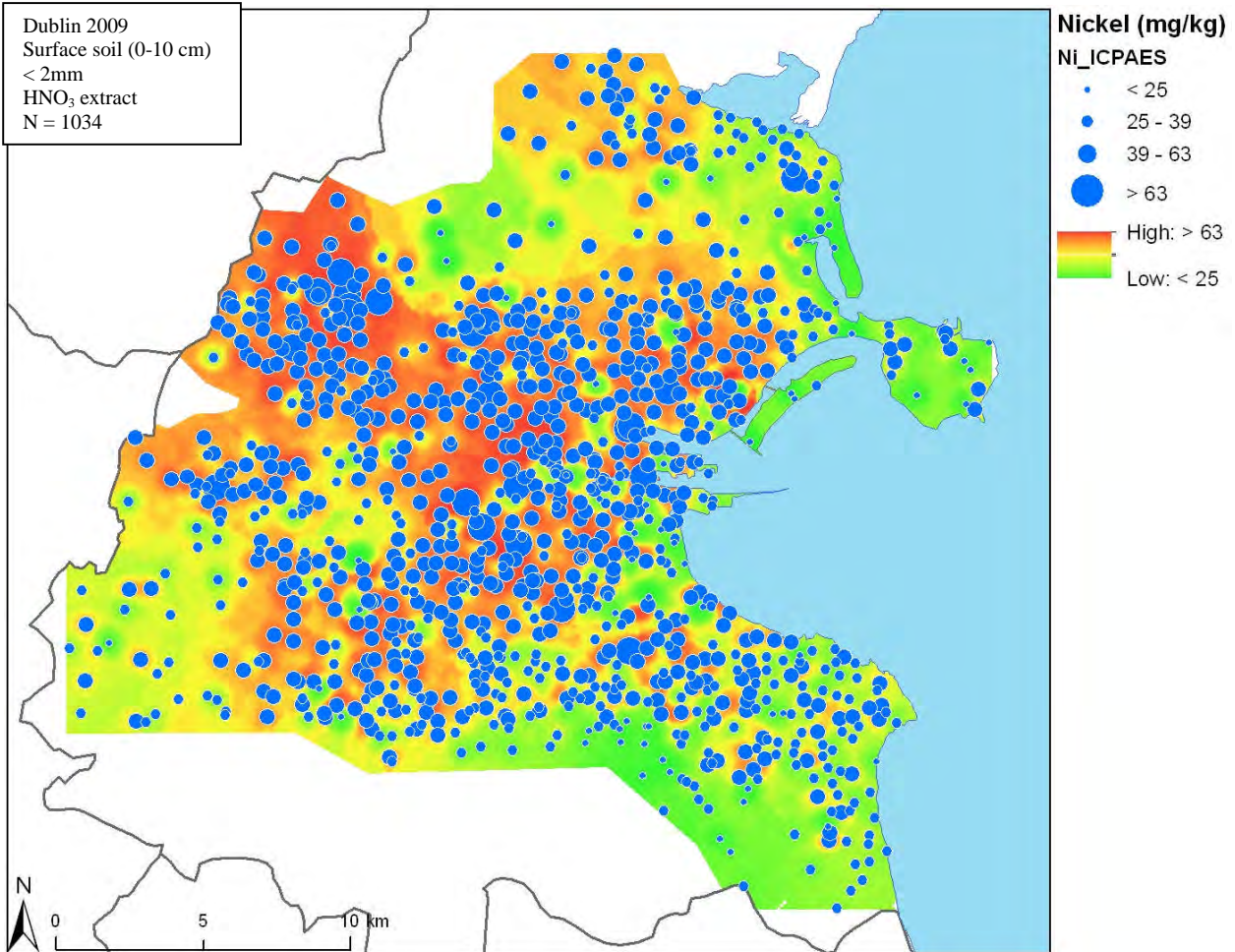
Mercury is for humans a non-essential metal. It occurs mainly in three different forms, as a metal, inorganic mercury salt and as organic compounds, mainly methyl mercury. Metallic mercury is volatile and detrimental to the central nervous system through inhalation. Inorganic mercury, for example mercury chloride, is taken up in the intestines and may damage the kidneys. Organic mercury is taken up in the same way and damages the peripheral nervous system in adults and the central nervous system in children, leading to reduced motoric and cognitive development. The significant source for methyl mercury and inorganic mercury compounds is food, especially fresh water fish, sea mammals and seafood. For those with amalgam fillings in the teeth, those will remain the main source of mercury.

### Results

The slightly elevated levels in the central parts of Dublin are probably attributed to anthropogenic sources. The natural mercury levels in surface soils in Dublin vary between 0.01 and 0.5 mg/kg, NSD-values 0.087 – 0.59 mg/kg.

DMR	Garda	N	Min	Median	Mean	Max
<b>Whole area</b>		<b>1034</b>	<b>0.01</b>	<b>0.21</b>	<b>0.35</b>	<b>24</b>
Northern	Coolock	110	0.04	0.15	0.17	0.55
	Raheny	80	0.02	0.23	0.33	2.8
	Santry	47	0.08	0.34	0.37	1.2
Western	Blanchardstown	158	0.01	0.17	0.26	1.5
	Clondalkin	82	0.02	0.18	0.20	0.93
	Lucan	51	0.02	0.14	0.16	0.51
North Central	Bridewell	16	0.18	0.92	0.86	1.5
	Fitzgibbon Street	14	0.09	0.49	0.64	1.5
	Store Street	20	0.02	0.20	0.41	3.3
South Central	Donnybrook	44	0.03	0.43	0.56	2.1
	Pearse Street	13	0.14	0.59	2.7	24
	Kevin Street	20	0.16	0.66	1.1	7.4
Southern	Crumlin	39	0.11	0.38	0.47	1.6
	Tallaght	114	0.05	0.21	0.26	1.3
	Terenure	34	0.08	0.41	0.47	1.9
Eastern	Blackrock	93	0.02	0.19	0.27	3.2
	Bray	24	0.05	0.12	0.16	0.76
	Dun Laoghaire	75	0.05	0.18	0.25	1.4





## Nickel (Ni)

### Sources

Nickel is being used in alloys (e.g. with iron, zinc, manganese, cobalt, titanium and molybdenum), electroplating, batteries, pigments, catalysts and magnetic tapes. Anthropogenic sources include copper-nickel smelters, steel works, chemical industry, petroleum refining, waste disposal, incineration, sewage sludge, fertilisers, traffic and fuel combustion (Reimann and Caritat, 1998).

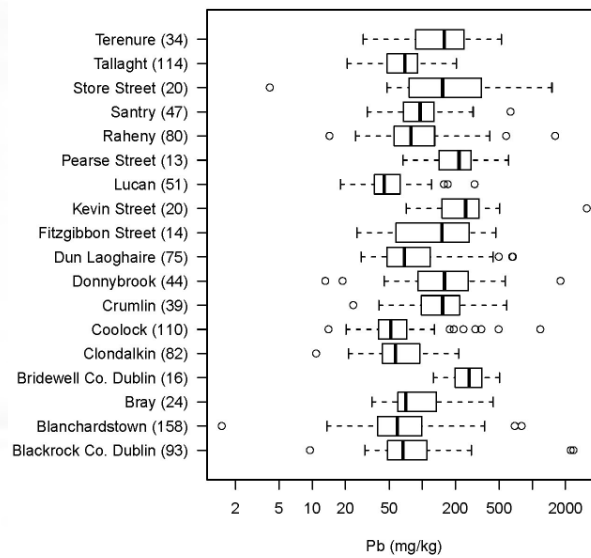
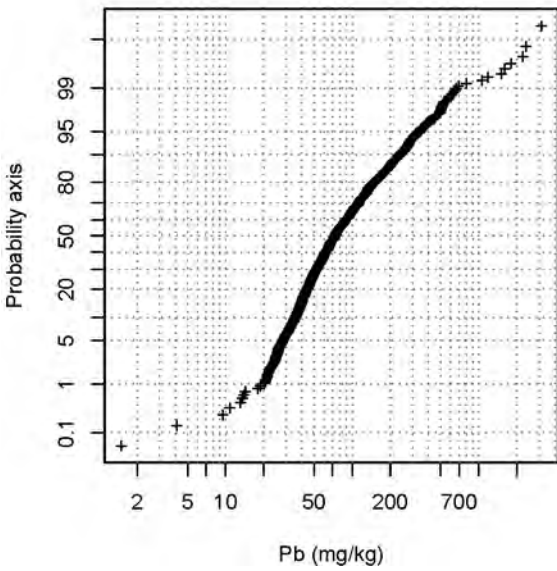
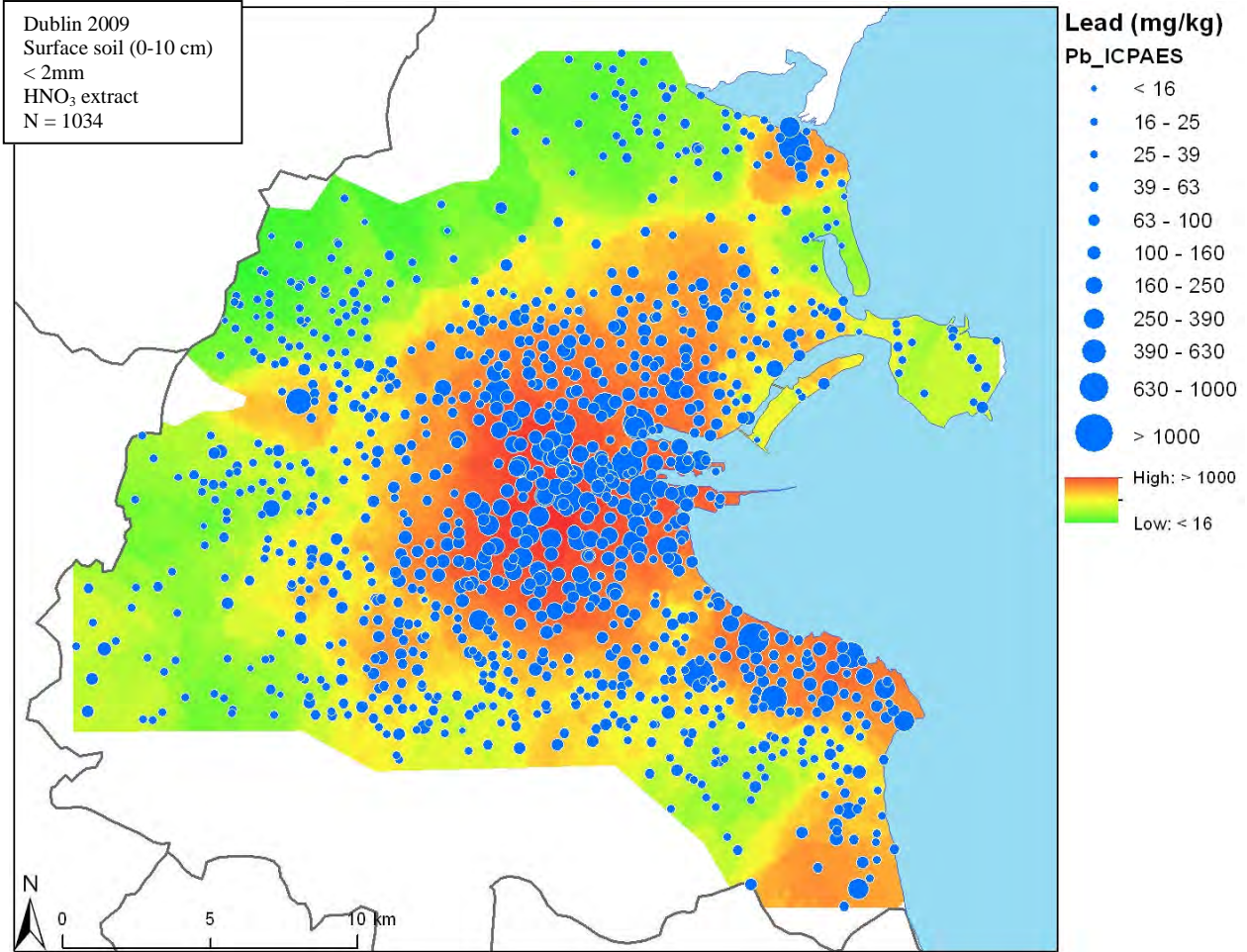
### Health

Nickel is for humans a non-essential metal. The main sources of nickel are from food made in cooking pots. Nickel causes cancer through inhalation, but not if taken up orally. Nickel may cause allergies through dermal contact.

### Results

Elevated nickel levels seem to correspond with the underlying impure limestone (Fay et al., 2007). Geology is the main source for nickel in surface soils in Dublin. The natural nickel levels in surface soils in Dublin vary between 5 and 55 mg/kg, NSD-values 11 – 50 mg/kg.

DMR	Garda	N	Min	Median	Mean	Max
<b>Whole area</b>		<b>1034</b>	<b>5.5</b>	<b>41</b>	<b>41</b>	<b>145</b>
Northern	Coolock	110	7.1	40	38	63
	Raheny	80	6.1	41	39	67
	Santry	47	20	43	43	56
Western	Blanchardstown	158	11	45	46	84
	Clondalkin	82	7.9	40	40	55
	Lucan	51	27	41	42	71
North Central	Bridewell	16	26	49	49	62
	Fitzgibbon Street	14	27	49	48	63
	Store Street	20	5.5	39	42	126
South Central	Donnybrook	44	9.6	42	39	62
	Pearse Street	13	21	45	43	61
	Kevin Street	20	31	45	50	145
Southern	Crumlin	39	28	46	45	64
	Tallaght	114	18	41	39	57
	Terenure	34	27	44	45	77
Eastern	Blackrock	93	11	37	36	66
	Bray	24	19	33	33	49
	Dun Laoghaire	75	17	34	35	50





## Lead (Pb)

### Sources

Lead accumulates in urban soil due to emissions from sources such as leaded petrol, metal industry and pigments in paint, plastic, glazed ceramics and roof tiles. Anthropogenic sources therefore include traffic, copper, zinc and lead smelting, steel works, battery factories, sewage sludge and waste incineration, as well as fires (Reimann and Caritat, 1998). In recent years, electronic wastes have also become a considerable source (Ajmone-Marsan and Biasioli, 2010). Due to the phasing out of leaded petrol, the lead emission levels have decreased from car traffic. In the urban environment, sources such as leaded paint, glazed pottery, bricks and roof tiles as well as glass will contribute to high levels of lead in the soil.

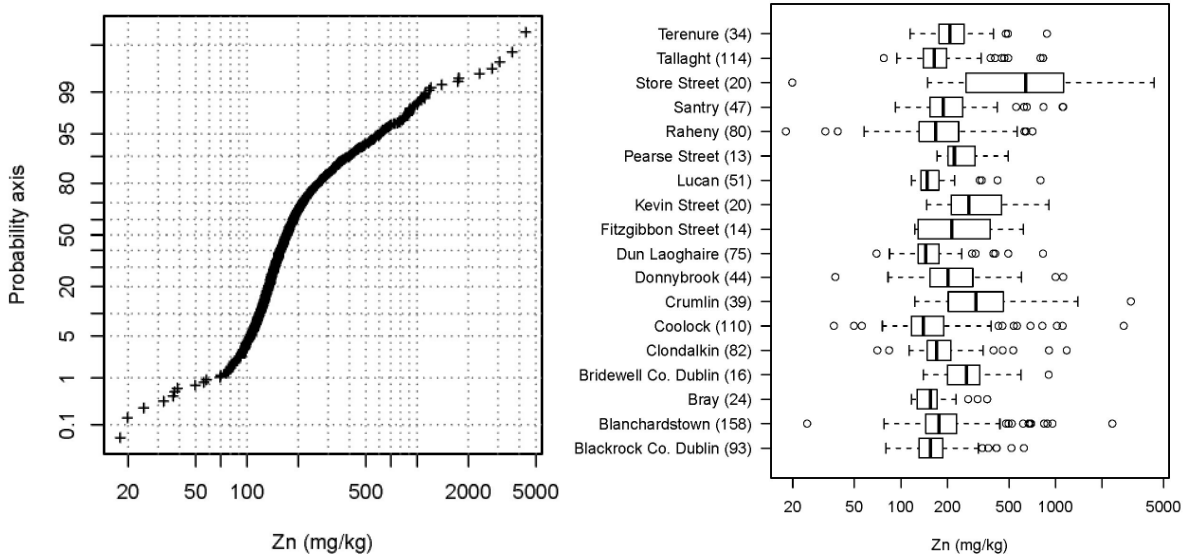
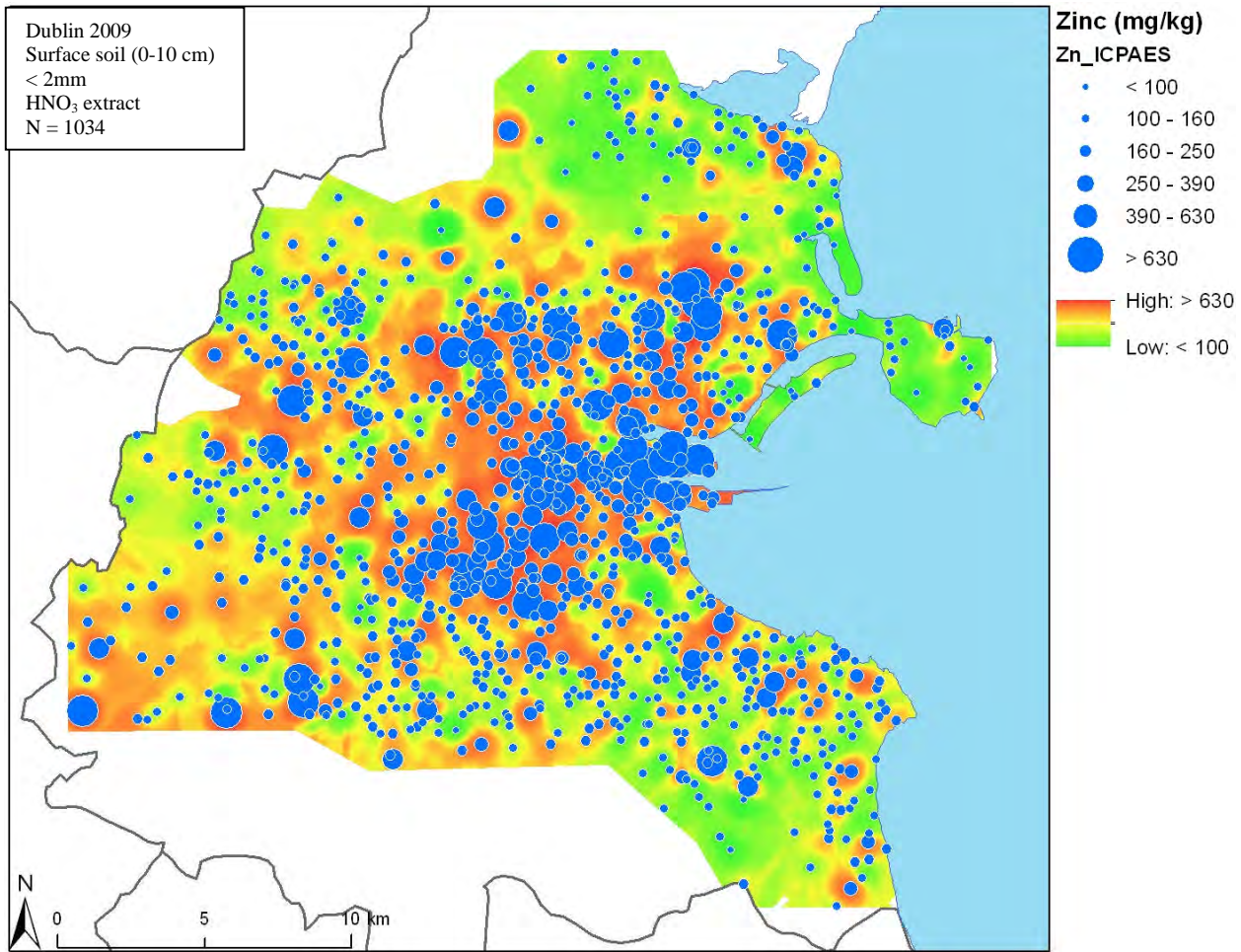
### Health

Lead is for humans a non-essential metal. In general, the main source of lead for humans is food, with lead accumulating in bones and teeth. Small children absorb it more readily than adults. Lead is toxic and damages the central nervous system for children, with the consequence of a reduced development of cognitive learning capabilities. High lead concentrations in soil have been proven to increase blood lead levels (Mielke, 1999; Mielke et al., 2005). Lead concentration levels of 300-400 mg/kg in soil give rise to blood lead levels of 10µg/dl, which is the threshold level for subtle health effects in children.

### Results

Lead presents a clear relation to the urban development of Dublin, where the highest levels are present in the central, oldest parts, which indicates mostly anthropogenic sources and not connected to the local geology. Local high levels in the outer parts of Dublin might be related to old towns and villages. The outskirts typically show low levels, apart from a hot spot in the Northeast, which is possibly caused by lead mineralisation. Nearly 35 per cent of the samples exceeds the Norwegian health based soil criteria for residential areas. The natural lead level varies between 18 and 110 mg/kg in the Dublin data, NSD-values 30 – 120 mg/kg.

DMR	Garda	N	Min	Median	Mean	Max
<b>Whole area</b>		<b>1034</b>	<b>1.5</b>	<b>73</b>	<b>122</b>	<b>3120</b>
Northern	Coolock	110	14	52	79	1180
	Raheny	80	14	79	123	1610
	Santry	47	32	95	117	633
Western	Blanchardstown	158	1.5	60	90	798
	Clondalkin	82	11	57	72	214
	Lucan	51	18	45	59	298
North Central	Bridewell	16	126	266	284	504
	Fitzgibbon Street	14	26	152	183	465
	Store Street	20	4.1	153	295	1510
South Central	Donnybrook	44	13	160	229	1800
	Pearse Street	13	67	216	236	611
	Kevin Street	20	71	248	385	3120
Southern	Crumlin	39	24	153	181	587
	Tallaght	114	21	69	75	204
	Terenure	34	29	158	187	523
Eastern	Blackrock	93	9.5	67	132	2360
	Bray	24	35	71	110	442
	Dun Laoghaire	75	28	69	114	665



## Zinc (Zn)

### Sources

Zinc is being used in galvanising, alloys, rubber industry, pigments, chemicals, paints, glass, plastics, lubricants, batteries, pesticides, pharmaceutical industry, fungicides and building industry. Anthropogenic sources include zinc smelting, combustion, traffic (e.g. tire wear), waste water and sewage sludge (Reimann and Caritat, 1998).

### Health

Zinc is an element that is essential for humans. The main source of zinc is from food. In cases where drinking water comes through corroded pipes, the water may contribute. Only very high levels of zinc in soil pose a risk to human health. The contribution from soil is in  $\mu\text{g/day}$ , while the contribution from food is in  $\text{mg/day}$ . Nearly 7 per cent of the samples exceeds the Norwegian health based soil criteria for residential areas.

### Results

The slightly elevated levels in the central parts of Dublin are probably attributed to anthropogenic sources. The natural zinc level varies between 20 and 200  $\text{mg/kg}$  in the Dublin data, NSD-values 69 – 205  $\text{mg/kg}$ .

DMR	Garda	N	Min	Median	Mean	Max
<b>Whole area</b>		<b>1034</b>	<b>18</b>	<b>171</b>	<b>240</b>	<b>4360</b>
Northern	Coolock	110	37	140	220	2760
	Raheny	80	18	168	208	709
	Santry	47	92	188	275	1120
Western	Blanchardstown	158	1.5	12.7	12.5	18
	Clondalkin	82	70	170	209	1180
	Lucan	51	117	148	178	799
North Central	Bridewell	16	140	266	318	902
	Fitzgibbon Street	14	123	214	263	621
	Store Street	20	20	648	992	4360
South Central	Donnybrook	44	38	202	265	1120
	Pearse Street	13	171	222	262	496
	Kevin Street	20	147	275	366	909
Southern	Crumlin	39	123	306	440	3070
	Tallaght	114	77	164	195	830
	Terenure	34	115	208	249	879
Eastern	Blackrock	93	80	155	177	624
	Bray	24	117	156	172	361
	Dun Laoghaire	75	70	145	174	829



## Polycyclic Aromatic Hydrocarbons (PAH)

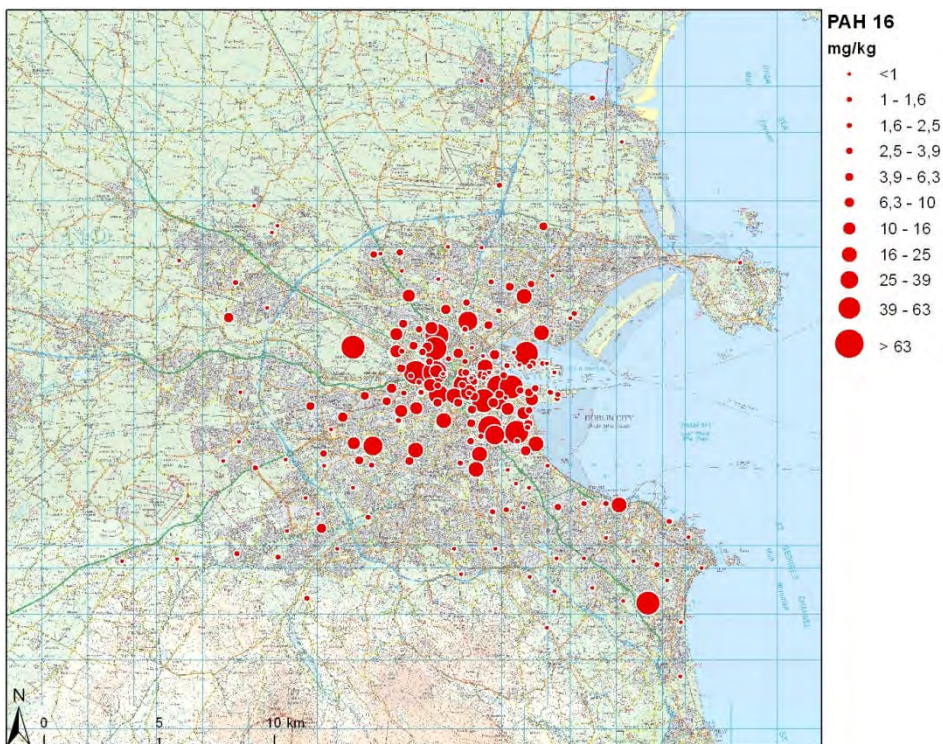
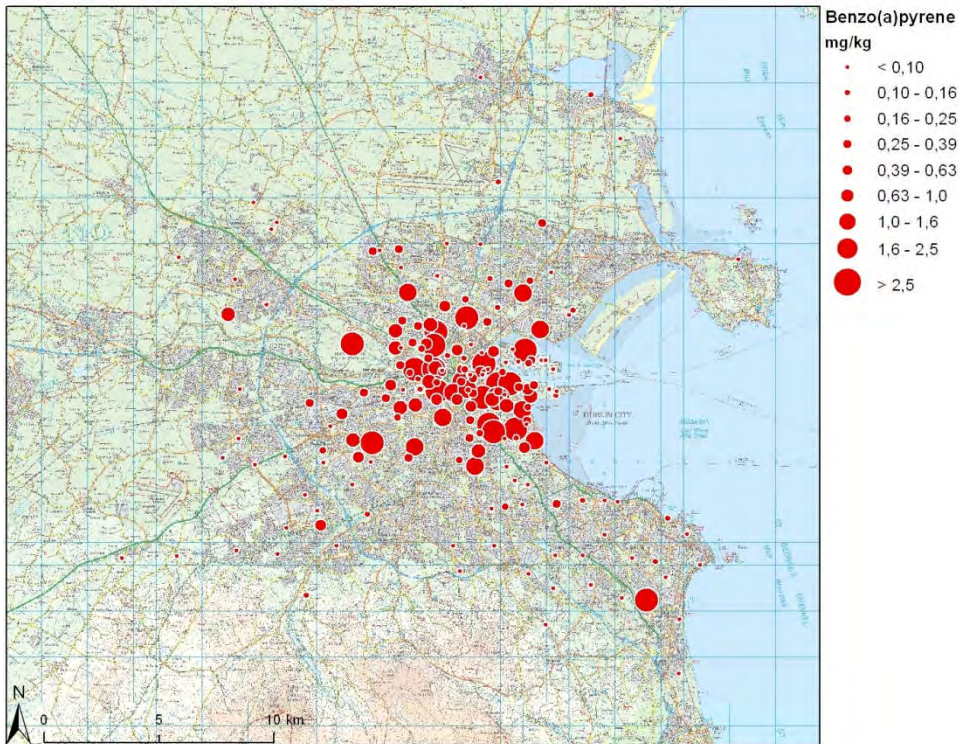


Figure 6. Maps presenting benzo(a)pyrene and PAH sum16.

### Sources

PAHs are complex mixtures of polycyclic aromatic hydrocarbons formed during incomplete combustion. Several hundred PAH-compounds have been identified. Of these, 16 are routinely determined in the laboratory. Typical domestic sources are heating using peat, coal and coke. Gasworks, cement production and other industry using coal or oil as their energy source contribute substantially. In addition, PAHs derive from emissions from engine combustion and the wearing of tires. Smoking is an important PAH source for humans in addition to food.

### Health

The PAHs are non-essential compounds to human beings. Several of the PAH compounds are carcinogenic and mutagenic (indicated in bold in the table below), where benzo(a)pyrene is the most carcinogenic of the PAHs that is usually reported. Uptake is typically through smoking, through air or through food, either taken up from the soil or from smoked foods, frying, cooking or barbecuing. Benzo(a)pyrene is then transformed to its metabolites that are known as highly carcinogenic and mutagenic. Exposure typically causes lung or colon cancer (Le Marchand et al., 2002). High prenatal exposure to PAH is associated with lower IQ and childhood asthma (US News, 2009).

### Results

The soils in Dublin inner city have high concentrations of all 16 PAH compounds that were determined. PAHs were detected across the city, with maximum concentrations occurring in the city centre (Figure 6). Concentrations decrease 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. It is likely that PAH concentrations in soils due to atmospheric pollution from coal burning will decline gradually over time in response to the bituminous coal ban put in place in Dublin in 1990.

Dublin (N=196)	Min	Median	Mean	Max	N<DL
Naphthalene	<0,015	0,015	0,083	2,4	110
Acenaphthylene	<0,015	0,015	0,123	3,9	108
Acenaphthene	<0,015	0,015	0,209	17	114
Fluorene	<0,015	0,015	0,245	26	113
Phenanthrene	<0,015	0,260	2,102	140	24
Anthracene	<0,015	0,057	0,557	50	75
Fluoranthene	<0,015	0,550	3,256	130	10
Pyrene	<0,015	0,530	2,748	92	10
<b>Benzo(a)anthracene</b>	<0,015	0,290	1,572	51	26
<b>Chrysene</b>	<0,015	0,370	1,639	44	12
<b>Benzo(b)fluoranthene</b>	<0,015	0,360	1,478	34	15
<b>Benzo(k)fluoranten</b>	<0,015	0,120	0,524	14	40
<b>Benzo(a)pyrene</b>	<0,015	0,260	1,140	28	21
<b>Dibezo(a,h)anthracene</b>	<0,015	0,047	0,199	4,4	82
Benzo(g,h,i)perylene	<0,015	0,220	0,773	14	22
<b>Indeno(1,2,3,cd)pyrene</b>	<0,015	0,200	0,747	12	29
Sum PAH(16)	<0,24	3,470	17,395	661,6	9
<b>Sum carcinogenic</b>	<0,075	1,600	7,297	190	23

## Polychlorinated biphenyls (PCB)

### Sources

Polychlorinated biphenyls (PCBs) have been found in a wide range of applications, including hydraulic oils, electrical transformers and capacitors, double-glazed windows, concrete constructions, sealants, plaster and paint (e.g. Sundahl et al., 1999; Hellman, 2000; Andersson et al., 2004; Herrick et al., 2004).

### Health

PCB is soluble in fat and degrades very slowly in nature. PCB is not acutely toxic but during chronic exposure, it accumulates in the body and affects the central nervous system and immune system. The main PCB-sources for humans are fish and seafood.

### Results

PCB's were found in 15 samples, where only 4 samples were higher than the detection level of sum PCB 7 (Figure 7). The samples were collected in parks, roadsides and open areas in Dublin. This indicates low levels of PCB in Dublin.

PCB whole Dublin (N=196) (mg/kg)	Min	Median	Mean	Max	N<DL
PCB Sum 7	<0,01	0,01	0,0106	0,0599	193
PCB-28 Trichlorobiphenyl	<0,0015	0,0015	0,0018	0,015	189
PCB-52 Tetrachlorobiphenyl	<0,0015	0,0015	0,0017	0,015	192
PCB-101 Pentachlorobiphenyl	<0,0015	0,0015	0,0016	0,015	195
PCB-118 Pentachlorobiphenyl	<0,0015	0,0015	0,0016	0,015	195
PCB-138 Hexachlorobiphenyl	<0,0015	0,0015	0,0017	0,015	189
PCB-153 Hexachlorobiphenyl	<0,0015	0,0015	0,0017	0,018	193
PCB-180 Heptachlorobiphenyl	<0,0015	0,0015	0,0019	0,023	187

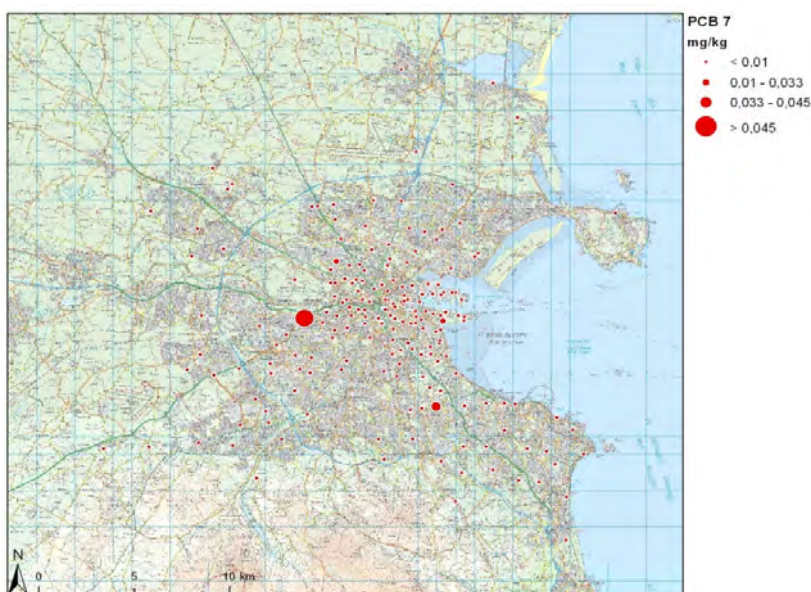


Figure 7. Map presenting PCBsum7.



## POSSIBLE SOURCES FOR LEAD AND PAHs IN DUBLIN

The contents of 32 metals, 16 PAHs and 7 PCBs have been mapped in the surface soils of Dublin. Generally, lead and PAH compounds are the only contaminants that may represent a health risk for the population. Possible sources for contamination by these compounds are discussed below.

### Lead

#### Leaded gasoline

The two “classical” lead sources are leaded gasoline and lead-based paint. Lead in gasoline was banned in Ireland in 1999, so this has been an important lead source up to that date (EPA, 2008) <http://www.epa.ie/downloads/pubs/other/indicators/irlenv/43366%20epa%20report%20chap%204.pdf>. Lead emitted from road traffic from the 1920 to 1999 is now stored in the surface soils.



Figure 8. Leaded gasoline was used until the ban in 1999.

### Leaded paint

Lead carbonate or lead sulphates were added to white paints in substantial quantities as the main pigment. These were added to paint products intended for use as a primer or top coat over metal and wood, both in interior and exterior paints. Examples of where this type of paint may have been used are skirting boards, doors, door frames, stairs, banisters, window frames and sills, wooden flooring, radiators, and pipes, though it could also have been applied to any other surface e.g. plaster walls during the time that lead was used for this purpose. Lead paint was banned, through an Act of Government (the 1991 Lead Act). Exterior paints are flaking off and enter the soils. In many American and European cities, including Dublin, this is an important lead source.

### Glazed roof tiles, pottery and leaded glass

A possible source for lead in central Dublin is glazed roof tiles which are commonly used. The glazed tiles contain many per cent of lead in the glaze (up to 60 per cent has been measured in Norway).



**Figure 9. A possible source for lead: these houses from central Dublin are shown as an illustration only. Glazed roof tiles and white painted window frames might have high concentrations of lead present. Photo: Henning Jensen**

There are several products where lead is still present as it is still allowed to add during new production of some products: paints with less than 1 per cent lead, glass, pottery and ceramics, consumer products of plastic. Fragments of glass were commonly visible in the surface soils on a large number of sample locations (Figure 14).



### Contaminated ground

Urban soils are dynamic, as masses are excavated and moved by truck continuously. This movement of masses represents an important process for the spreading of contaminants in the urban environment.

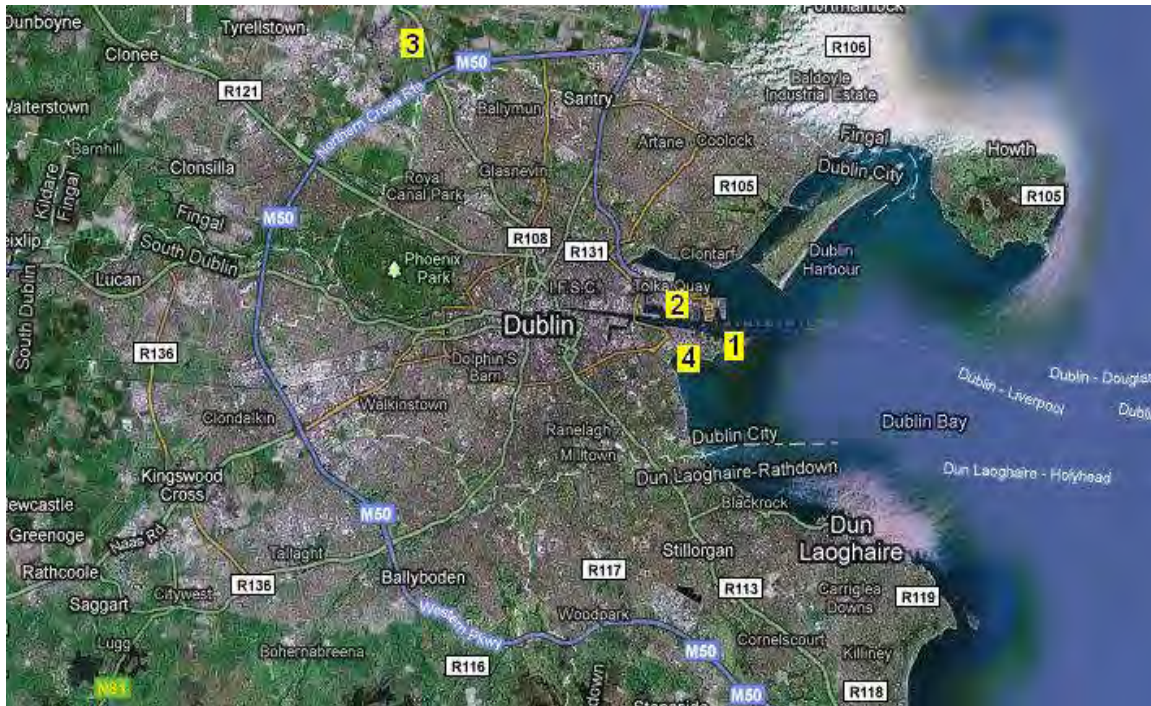
### **Polycyclic Aromatic Hydrocarbons (PAH)**

PAHs are formed during incomplete combustion of organic matter in domestic fires, industry and vehicle engines. PAHs emitted from combustion can travel long distances in the atmosphere and be deposited in soils. PAH contamination is also associated with fuel oil spills and creosote. PAH compositions indicated that the highest values of PAH's were generally found in the city centre of Dublin. PAH-profiles and box plots show that there were a higher number of light compounds present in central areas of Dublin than in the other regions. This is a strong indication that active sources of PAH-pollution still exist in Dublin today, since the lighter compounds are more easily bacterially degraded, water soluble and lost through evaporation compared to the heavier, 4 – 6 ring, PAH compounds.

### Gasworks and domestic heating

In the 1870's there were five glassworks in Ringsend, which used large quantities of coal to manufacture glass (DDDA,2010). Other major contributing factors could be the coal and turf burning in private household, traffic and garbage burning around the city.

The coal industry, which consisted of coal merchants, gas works and organic chemical works were centred on the Grand Canal Docks areas of the docklands. Coal gas was used to light street lamps and local homes in the 19<sup>th</sup> century. Coal gas is produced during coal carbonisation, which is the high temperature combustion of bituminous coal in anoxic conditions (UK DoE, 1995). Also produced during coal carbonisation is coke (a type of smokeless char used in metal works furnaces), coal tar (used as a source of organic chemicals), clinker or fused ash waste, lime and ammonia (both used to purify coal gas) (UK DoE, 1995).



**Figure 10. Gas works in and energy production sites in Dublin: (1) Poolbeg, (2) North Wall, (3) Hunstown and (4) Synergen.**

### Industrial emissions

Industries which emit PAHs to the environment typically include waste incineration plants, hazardous waste sites, metal works and wood-preserving facilities (ATSDR,1995a).

Industries which burn fossil fuels or organic matter typically emit PAHs to the air. Industrialisation began in Dublin in the mid to late 19th century. Dublin did not become heavily industrialised during this time, most industry was located in the docklands and was related to shipping, exports, and the distribution and processing of imported goods (DDDA, 2010). These 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.

Coal carbonisation is associated with coal combustion emissions to the atmosphere and ground contamination from by-products, coal tar lagoons and coal dust. By-product waste materials such as clinker and lime were often used as hardcore fill materials at gasworks sites (UK DoE, 1995a). Many such industrial waste materials were used historically to progressively reclaim land in Dublin's docklands area during industrialisation in the 19th and early 20th centuries.

The Grand Canal Docks area had suffered serious organic chemical contamination as a result of the coal industry and was extensively remediated and redeveloped for commercial and residential use in the 1990s and 2000s. 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). In Ireland electricity generation traditionally relied on the combustion of peat, coal and fuel oils. 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, 1995).

Historically, coal stockpiles were stored directly on the ground and ash was reused as fill on site (UK DoE, 1995). In 2009, the Electricity Supply Board (ESB) operated 25 power generation facilities in Ireland, of which 10 are run by hydroelectric power, 7 by gas/coal/oil, 6 by wind power, and 2 by peat (ESB, 2009). One remaining station at Moneypoint, Co. Clare is coal-fired. Dublin's three ESB stations are located in the docklands area, one at North Wall and two at Poolbeg. Poolbeg (Ireland's second largest power station after Moneypoint) has a long history of coal-fired power generation stretching back to 1903 (Bunbury, 2009).

The current Pigeon House facility, with its two distinctive smoke stack chimneys, runs on oil or gas. The independent gas-fired Synergen plant operates at the same site. The North Wall Quay 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.

### City fires

The occurrence of city fires is another source for pollutants including both PAH and heavy metals: One major city fire took place in 1866 (<http://www.chaptersofdublin.com/>). The fires cause emissions and leave burnt out remains and high concentrations of several pollutants in the ashes on the ground. These will be spread to the soil through demolition work.

### Private burning of waste

Private burning of waste was observed in open spaces and parks during the field work in Dublin (Figure 11). It is a small and local source for PAHs, but the extent of burning domestic waste can be expected to rise during times of economical recession.



**Figure 11. Domestic burning of waste.**

Vehicle engines combustion (cars, trains, ships)

These are typical urban PAH-sources. In addition to the emissions from the engine, also the tires contain PAHs which enters into the environment.

Other potential sources of PAH concentrations in Dublin soils include contaminated fill materials in reclaimed land, bonfires and creosote treated wood.

## **METHODS**

### **Planning and preparations**

The initial planning of the sampling period was done in conjunction with GSI. The strategy used when choosing sample localities was to use a 1 km<sup>2</sup> grid, as it had been previously determined that the sampling density would be 4 samples/km<sup>2</sup> in densely populated areas and 1 sample/km<sup>2</sup> in more sparsely populated areas in the outer parts of Dublin. The densely populated areas were determined using spatial information provided by GSI. Aerial photos/ortho photos with 1 km × 1 km grids supplied by GSI were used in the field together with lists of locations for sampling. Taxis were used during sampling, increasing sampling efficiency through reduced travelling time between sampling locations. Dublin street maps (scale 1:20 000) were used for easier location of streets and parks. The project budget did not allow for analysis of PCBs and PAHs (POPs) of more than 200 samples; requiring a separate sample. Inner city locations were prioritized for this type of analysis, but with a flexibility allowing for some samples also in the suburbs and rural districts, depending on the judgment of the experienced field crew.

### **Sampling**

Soil samples were collected from a total of 1034 locations from publicly owned land areas starting from the 23<sup>rd</sup> of October to the 3<sup>rd</sup> of November, 2009 (Figure 13). Land use types that were sampled include: open space (227), parks (423), road verges (214), schools (42), sports grounds (60), playgrounds (13), private residential gardens (3), allotments (2). Sampling was restricted to publicly owned land. Samples for PAH and PCB were sampled at 196 locations, prioritizing inner urban areas relative to outer urban areas (Figure 12). Duplicate samples were collected at every 30<sup>th</sup> location. This was done in order to test reproducibility.

All samples were single samples collected from surface soil (0-10 cm). Approx. 400 gram of soil was sampled from each location. The shovel was cleaned between sample stations. Where the sampling was done in grasslands or lawns, the grass was removed and the soil including the roots was extracted/sampled. Figures 14, 15 and 16 illustrate examples of sampling sites.



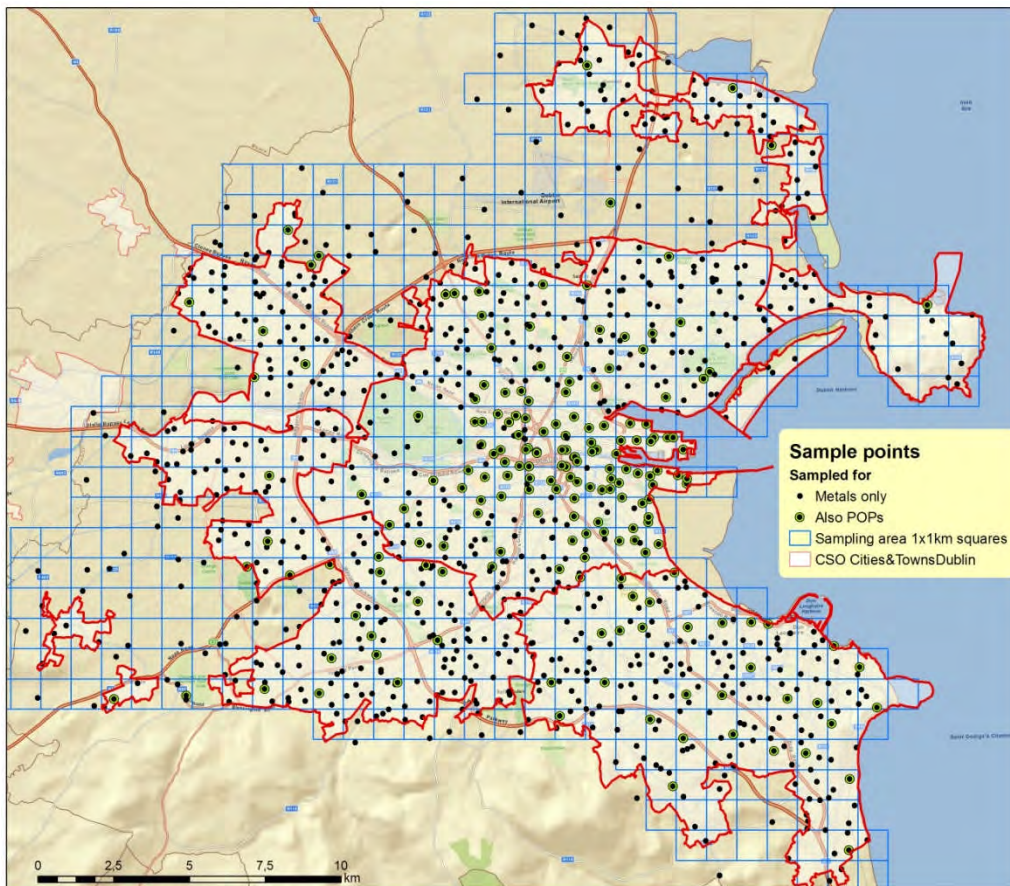


Figure 12. Sample sites in Dublin (N= 1034). The samples analysed for organic pollutants are indicated with a green ring.

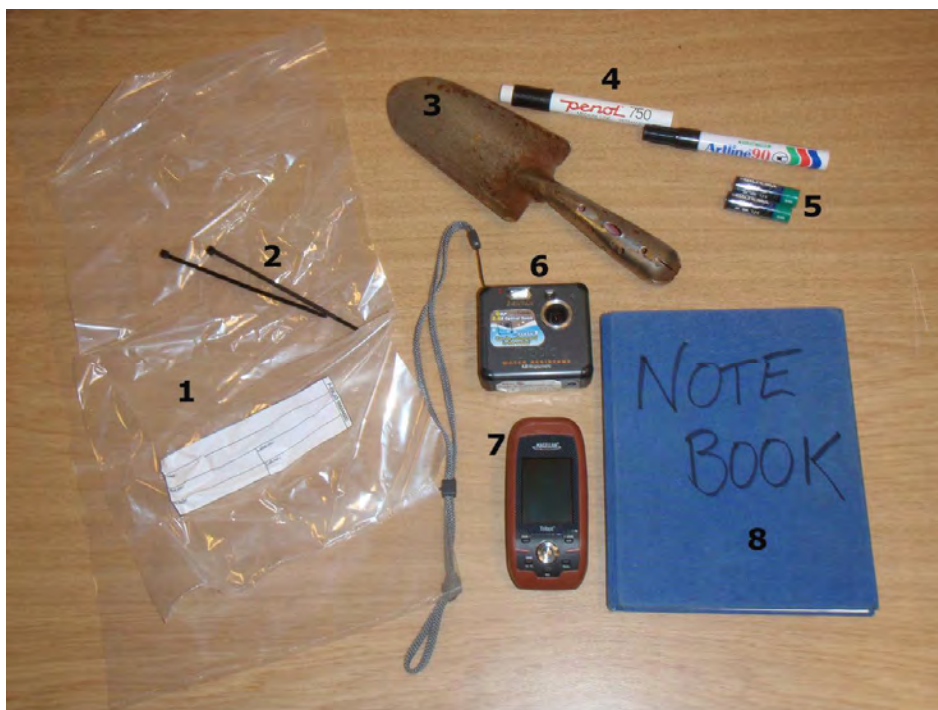


Figure 13. Sampling equipment comprising of Rilsan® sample bags (1), strips (2), handheld shovel (3), waterproof marker pens (4), extra batteries for the GPS (5), digital camera (6), GPS (7) and notebook (8).





**Figure 14. Man-made particles, such as glass fragments, are common in urban surface soils in Dublin.**



**Figure 15. Coal-particle in surface soil will give high concentration of PAHs.**



**Figure 16. Typical sampling sites. Different types of sample locations including parks (a), open space (b), sports grounds (c), road verges (d), schools (e), playgrounds (f), private residential gardens (g) and allotments (h).**

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

Triplicate samples were taken at selected sample stations by other sampling teams. The analysis of these samples was done in order to test the variability when other sampling teams took the sample at an earlier sampled station compared to ordinary duplicate samples that were taken by the same field team.



## Sample preparation and chemical analyses

### Inorganic analysis

The samples for inorganic analysis were air dried at <math><30^{\circ}\text{C}</math>/ambient temperature and sieved through a 2 mm nylon sieve. The analytical work was undertaken on the <math><2\text{mm}</math> sieve fraction. The chemical analysis for the samples was done at the Geological Survey of Norway. The samples are digested by acid extraction in a microwave system, UltraClave IV, Milestone. 1 gram sample material was weighed into a PTFE vessel before 15 ml 7 N  $\text{HNO}_3$  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  $250^{\circ}\text{C}$ .

The acid extractions from the samples were filtrated using Whatman folded filters,  $\varnothing 90\text{ mm}$ . 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 inductively coupled plasma-atomic emission spectrometry (ICP-AES) instrument Perkin Elmer Optima 4300 Dual View. Loss of ignition was determined by heating the samples in  $480^{\circ}\text{C}$  for 20 hours. Generally, the detection limits for the elements are (mg/kg): Si (375), Al (30), Fe (4.5), Ti (1.5), Mg (150), Ca (150), Na (300), K (150), Mn (7.5), P (15), Co (0.15), V (1.5), Mo (1.5), Ba (1.5), Sr (1.5), Zr (3), B (15), Be (0.15), Li (0.75), Sc (0.15), Ce (3), La (0.15), Y (0.15), As (3), Cd (0.15), Cr (0.3), Cu (1.5), Hg (0.0075), Ni (1.5), Pb (3) and Zn (3).



**Figure17. ALcontrol laboratory in Sweden determined the content of PAHs and PCBs in 196 samples.**

### Loss on ignition (LOI)

LOI was determined as an indicator of organic matter. LOI was determined by heating the samples in  $480^{\circ}\text{C}$  for 20 hours and by gravimetric methods.

## Organic pollutants

### Polycyclic Aromatic Hydrocarbons (PAH)

Ten grammes of the soil samples were weighed and extracted using a 1:1 volume mixture of acetone and n-hexane. Determination of the 16 EPA PAH compounds was carried out using gas chromatography – mass spectrometry (GC-MS).

### Polychlorinated Biphenyls (PCB)

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

## **Quality control**

The field duplicate samples were treated as ordinary samples through sampling, sample preparation and chemical analysis. The field duplicate variance expresses the total variance and includes field sampling variance, laboratory sampling variance and variance due to detection in the ICP-AES instrument. Two natural standards were inserted at every 50<sup>th</sup> sample for the inorganic analyses to insure correct concentration level determined of the inorganic elements.

The elements sodium, molybdenum, silicon and boron, were rejected due to high detection limits or due to poor reproducibility between duplicate samples. The poorest reproducibility among the accepted elements was found with arsenic and lead, probably due to variations in the analytical process. The field duplicates showed a generally good dataset quality, where potential errors from within sample sites are small compared to the geographical variance between sample sites.

The influence or correlation of organic matter content on metal concentrations was checked through correlation analysis, using log-transformed results.

Further information on quality control is presented in Appendix 1.

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**APPENDIX 1:  
DETAILED QUALITY CONTROL/ASSESSMENT**

The quality assessment of the process ending up with the data set used for this report is enabled by a number of procedures during field, sample preparation and analysis.

### **Field positioning.**

The use of high quality GPS units incorporating D-GPS by the Egnos/WAAS option should, in principle, produce reliable coordinates (+/-5m 95%) for all sampling locations. To reduce the effects of (in principle unavoidable) malfunction, operator errors or poor dilution of precision (DOP) values ("urban canyon" and satellite geometry), all recorded positions were checked by GIS against orthophotos and where applicable, verified by inspection of field photos. An estimate of position error is reported in the original data file, suggesting an average error of 10m. This relatively high average value is mostly due to about 5% of the coordinates (almost all in rural districts) are given an error estimate of 100m for confidentiality reasons.

### **Reproducibility.**

Field teams collected duplicate samples from 30 of the ordinary sampling locations throughout the area. The duplicates were sampled concurrently with the ordinary samples, by the same team, but from a separate pit typically 1 – 10 m apart. The samples were treated as ordinary samples in the workflow, and the analytical results are used for the scatter plots presented below. In the scatter plots, the results of the ordinary sample are plotted along the X-axis, and the duplicates along the Y-axis. Ideally, the points should plot along the diagonal through 0,0, and deviations from this line is a graphical display of the sum of errors involved with almost all steps from field to report. The  $R^2$  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. It must, however, be taken into consideration that the matrix sampled is urban soil, which is more heterogenous than natural soil. Hence, a larger error margin should be expected, and geographical clusters should be emphasized rather than single points only.

All elements show acceptable reproducibility. No plots are made for Si, as the procedures are not certified for HNO<sub>3</sub>-extraction of geologic material. One of the field duplicates (2218, see plot for Ba) shows high deviation for a number of elements. A repeated weighing, extraction and analysis of the pair confirmed the deviation.

### **Systematic errors and creating tie-in points for other work.**

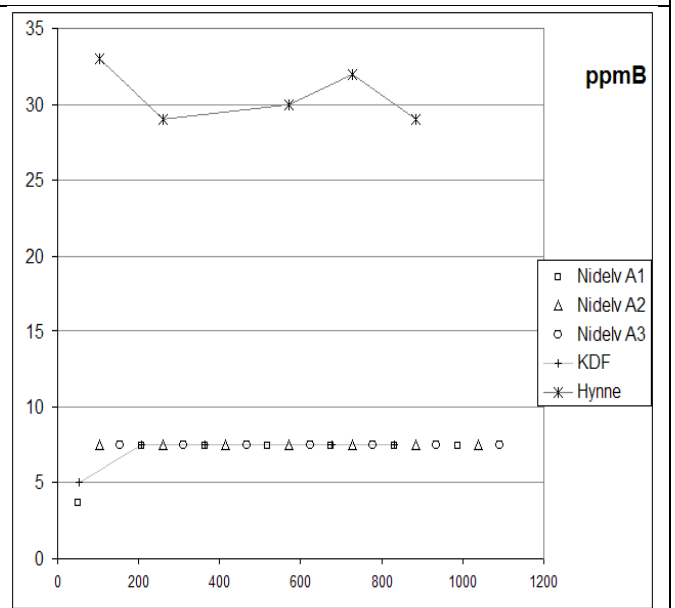
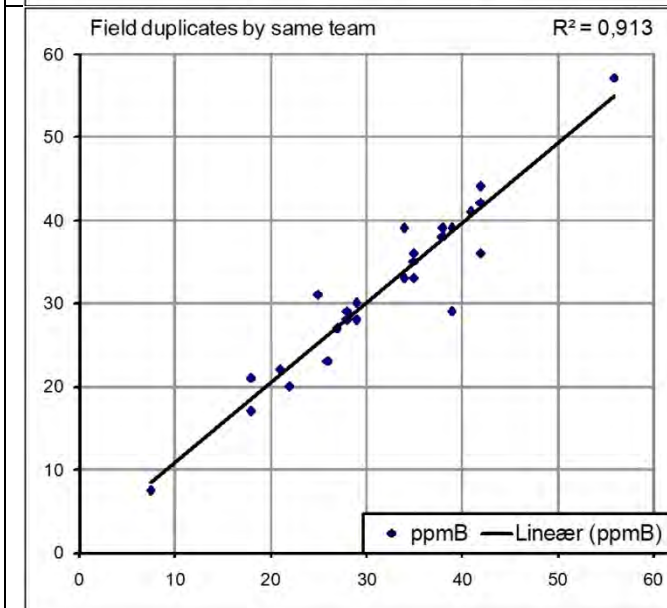
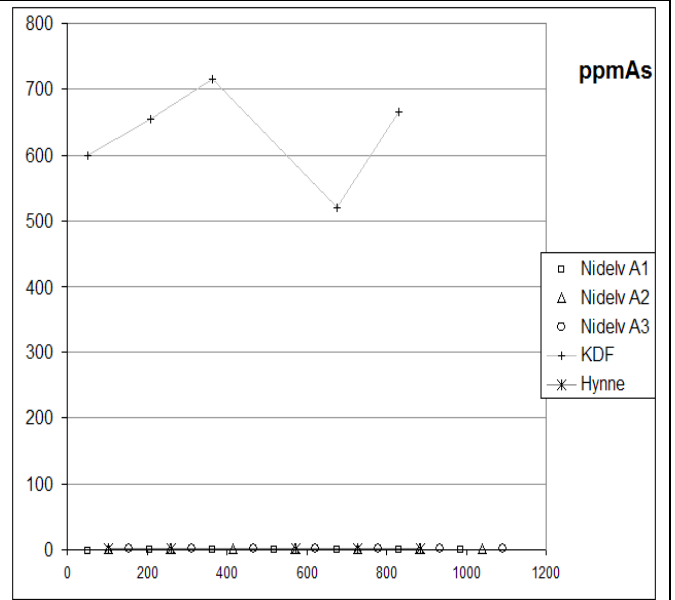
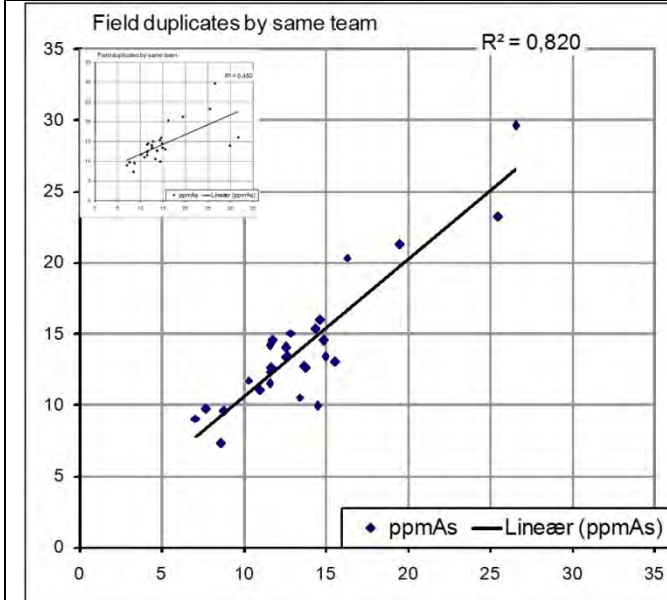
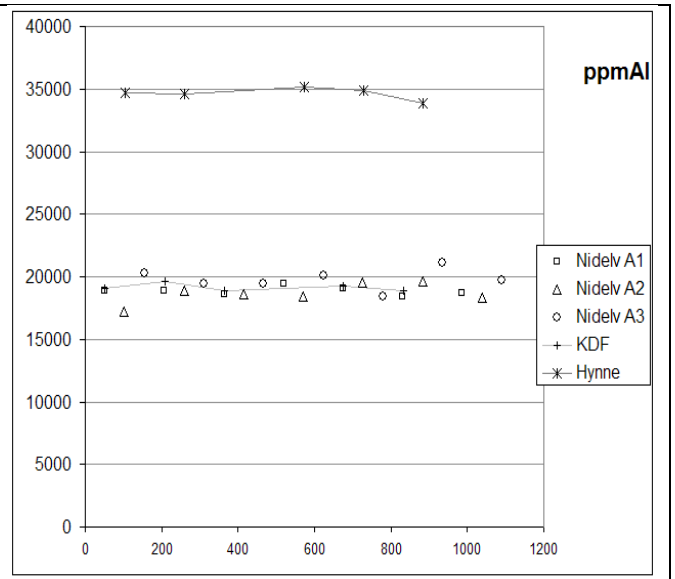
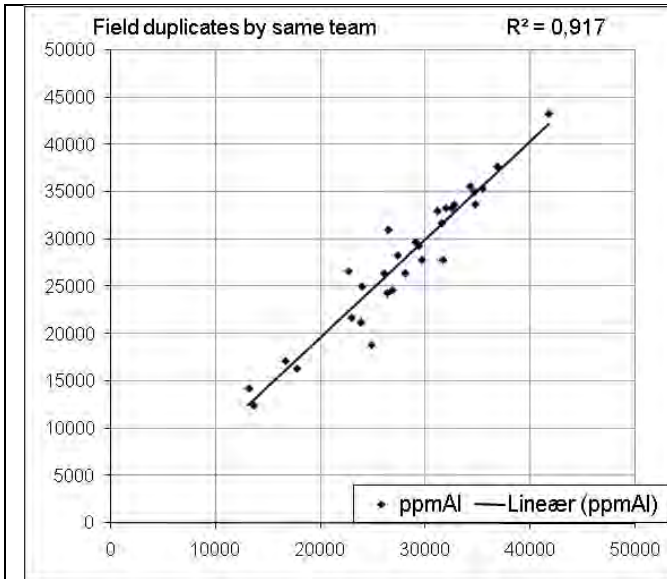
The time span from start to finish of the preparation and analysis of a 1000+ sample set is quite lengthy, and increases the chance of systematic errors occurring during the extraction and analytical steps. To monitor analytical levels throughout the data set, in-house natural material standards were introduced throughout the sample batch prior to analysis. 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.

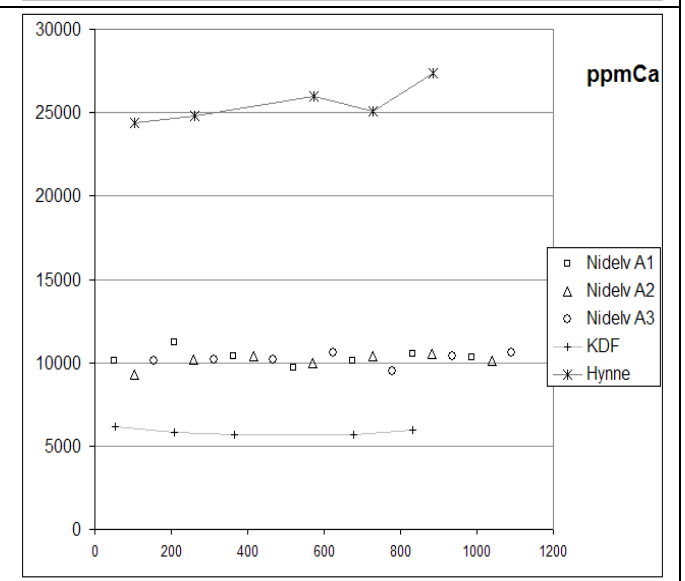
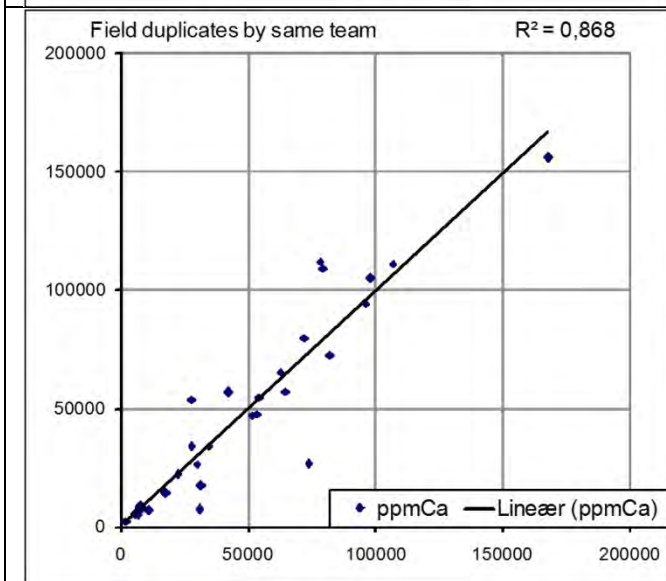
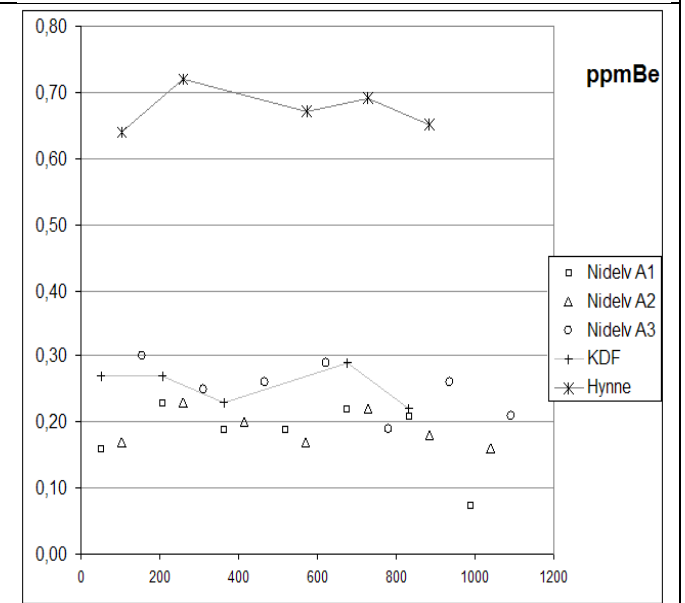
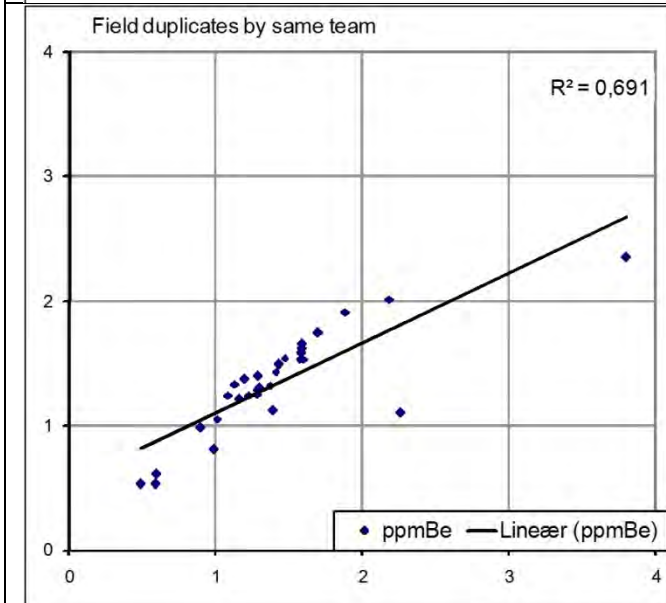
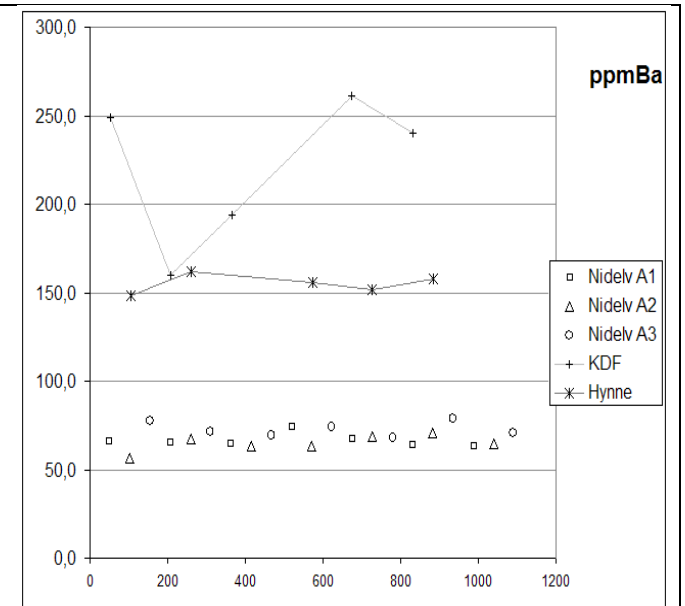
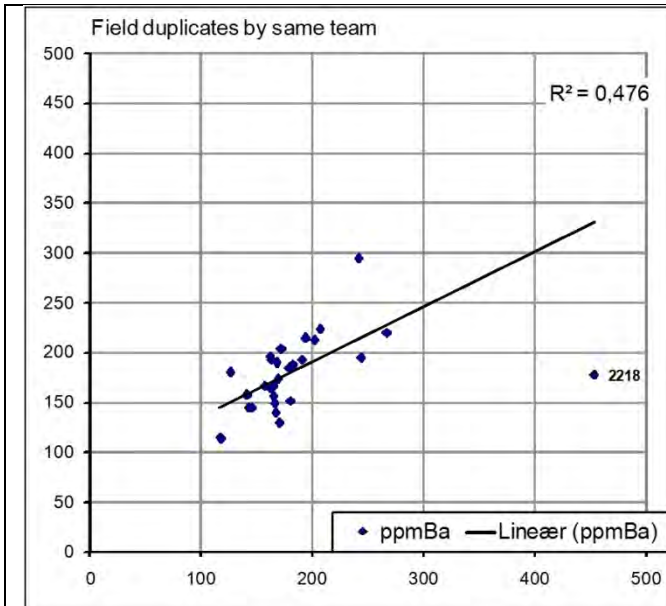
When assessing the results of the standard samples, no elements indicate systematic errors.

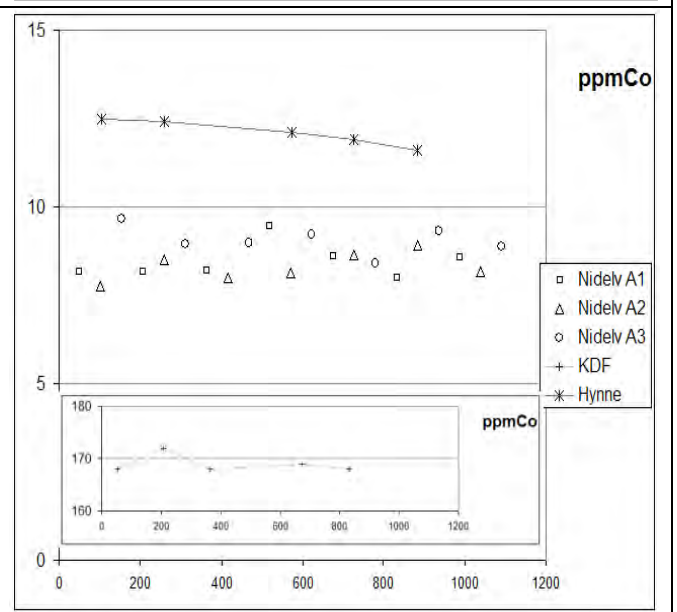
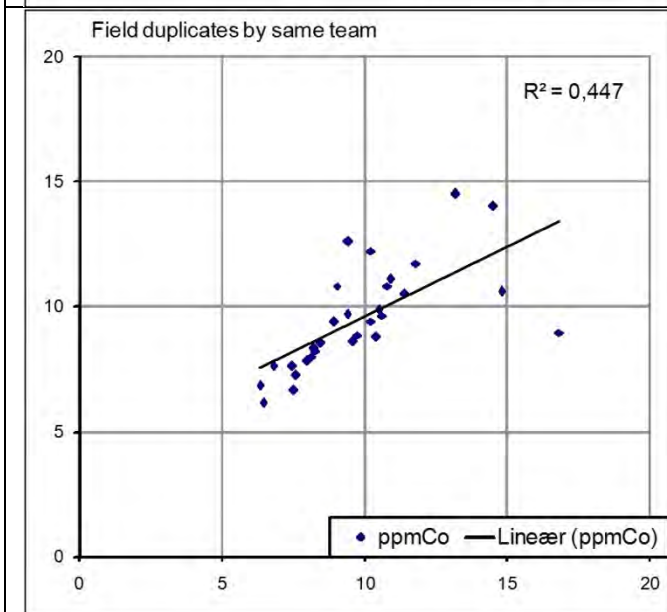
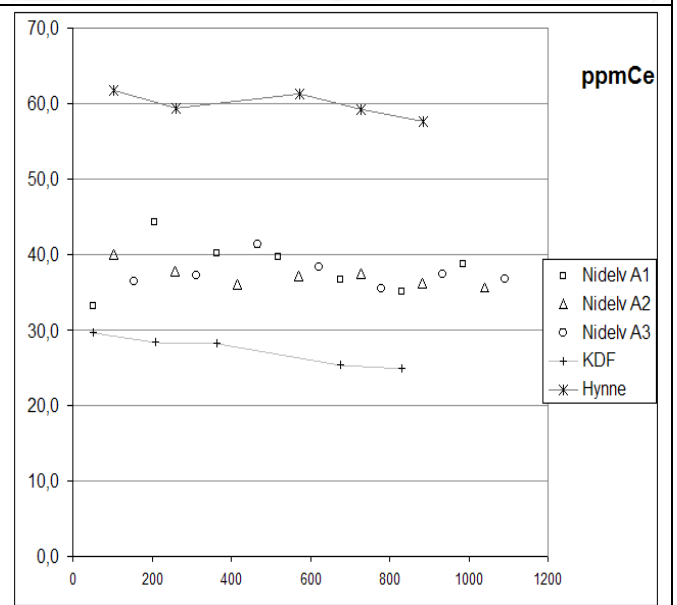
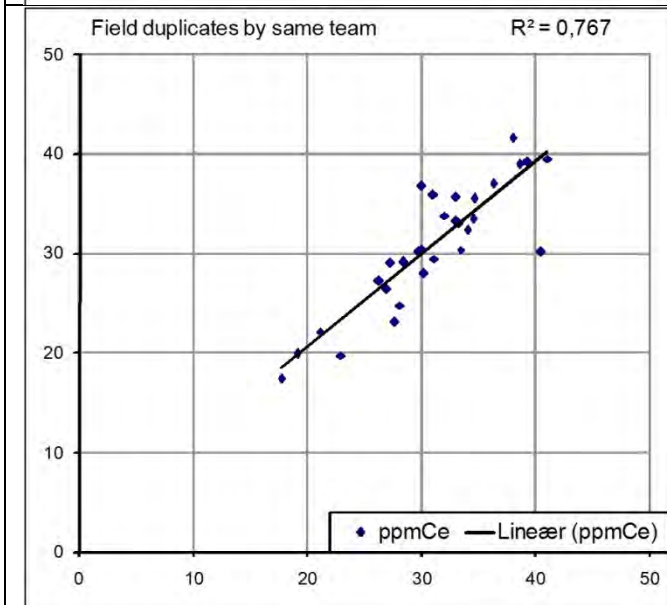
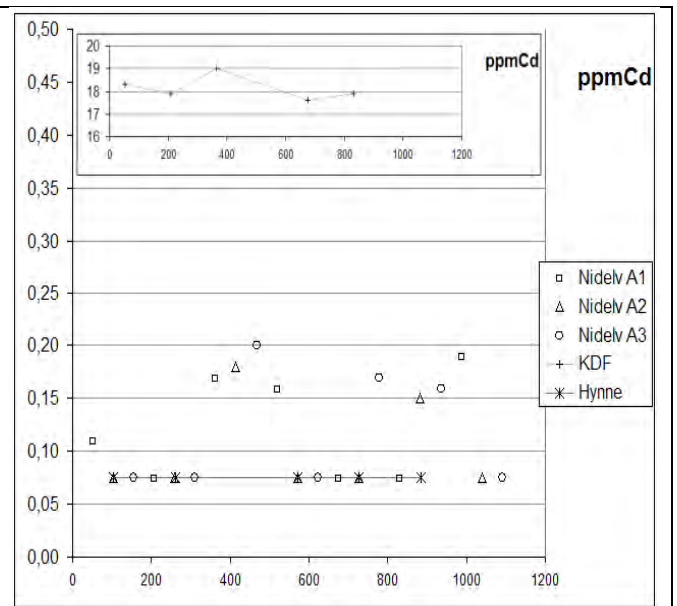
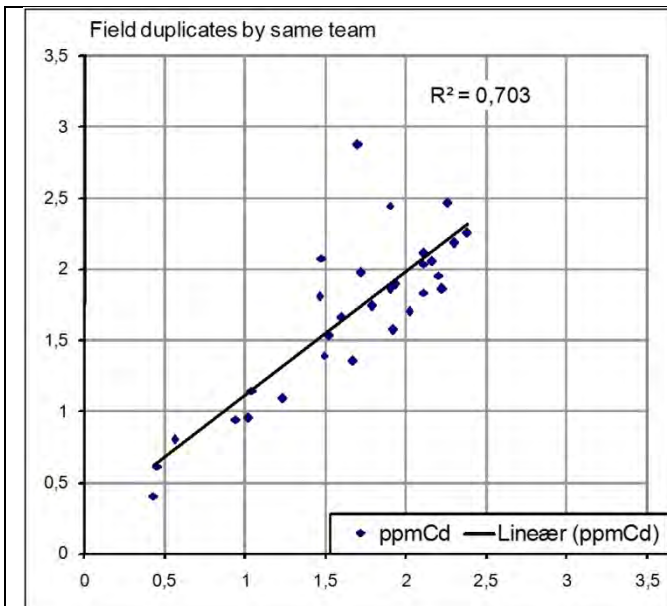
**Accuracy.**

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

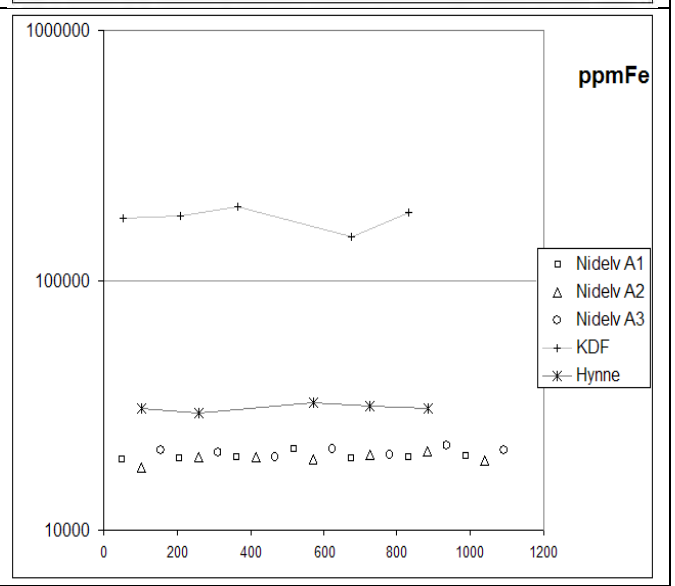
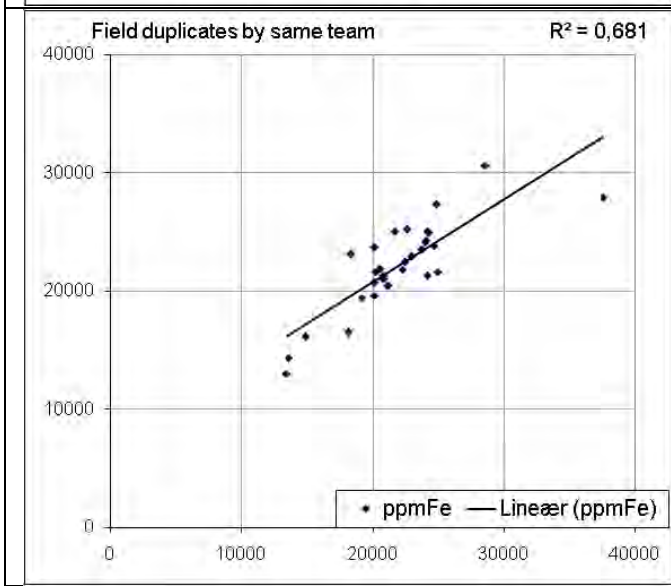
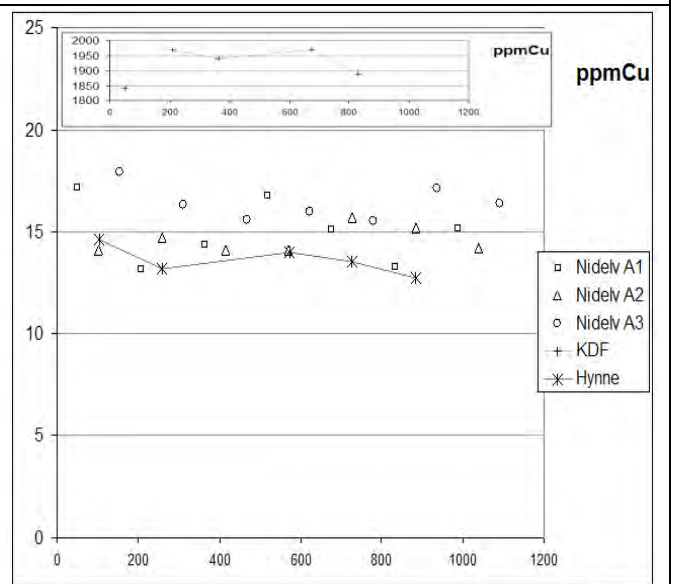
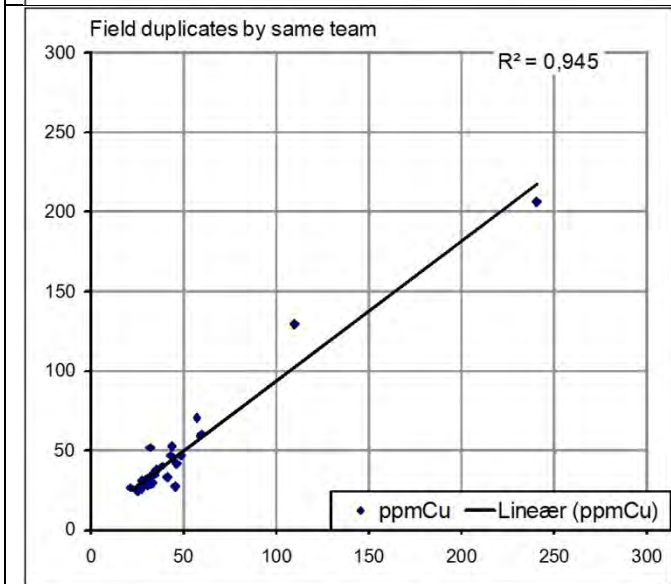
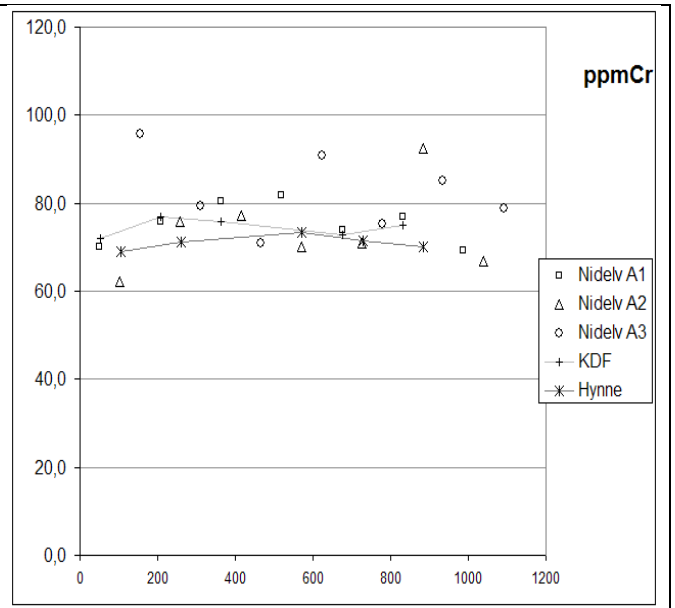
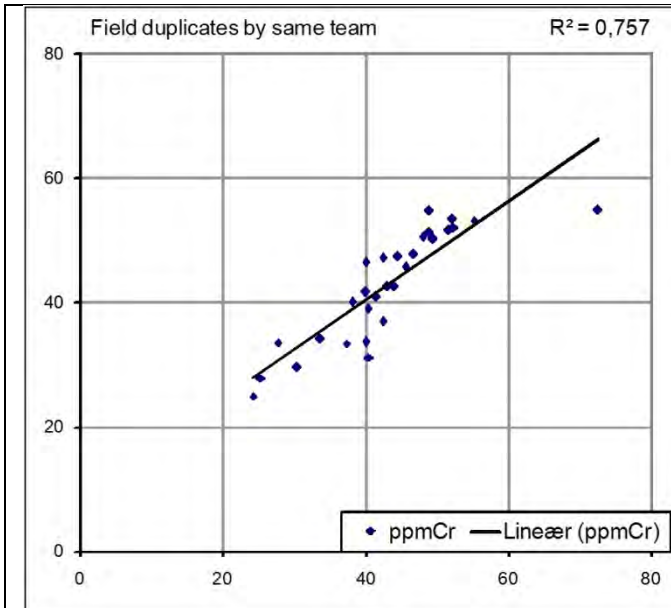
The reported values for Mo give rise to unacceptably high RSD. The concentration of Mo in the acid extract from MESS-3 is, however, near the detection limit of the method. Uncertain accuracy for Mo is the consequence, even though field duplicates show acceptable reproducibility. Due to the lack of accuracy information, Mo is left out of further processing.

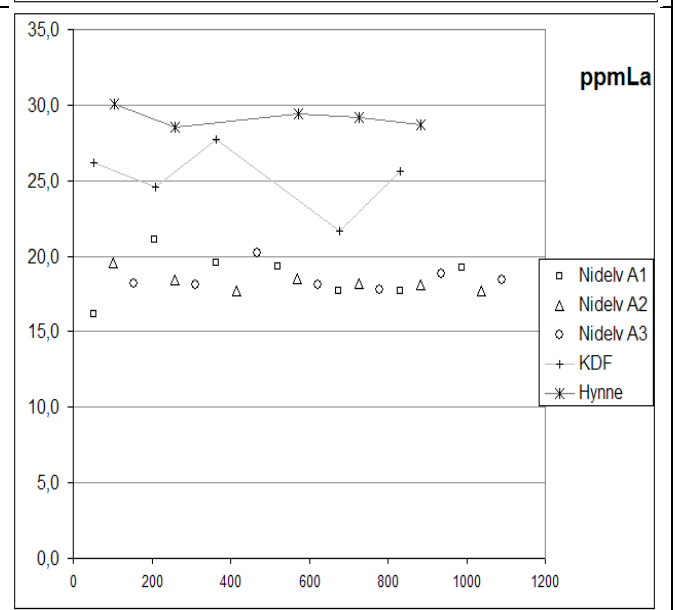
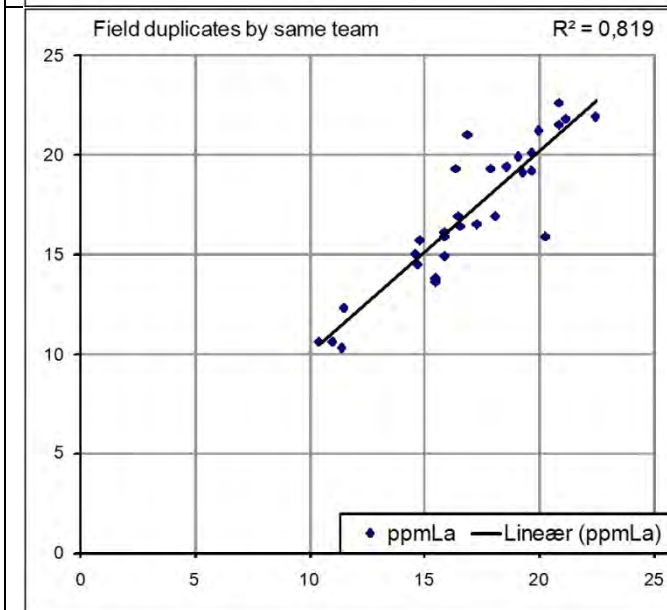
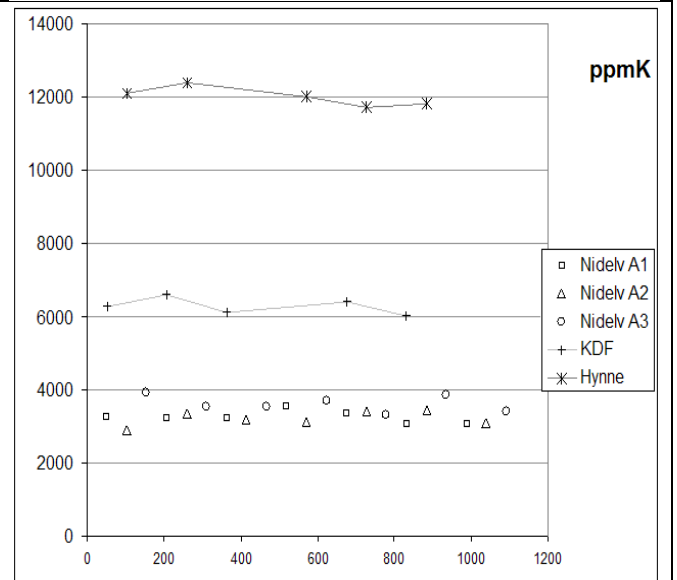
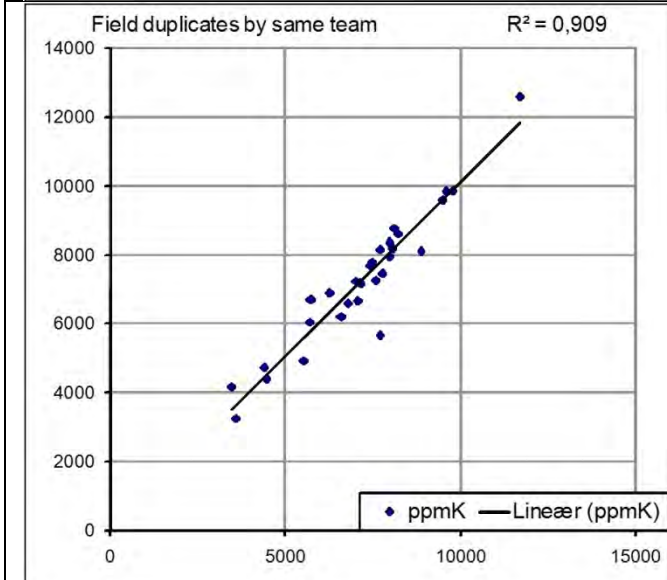
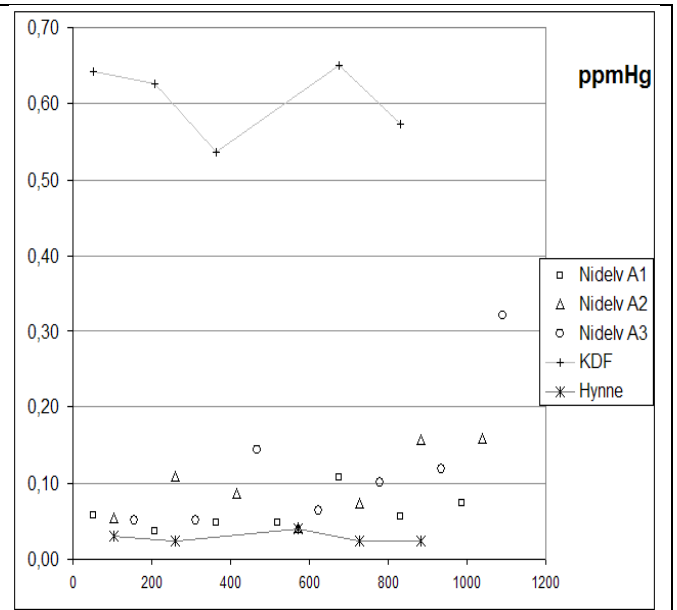
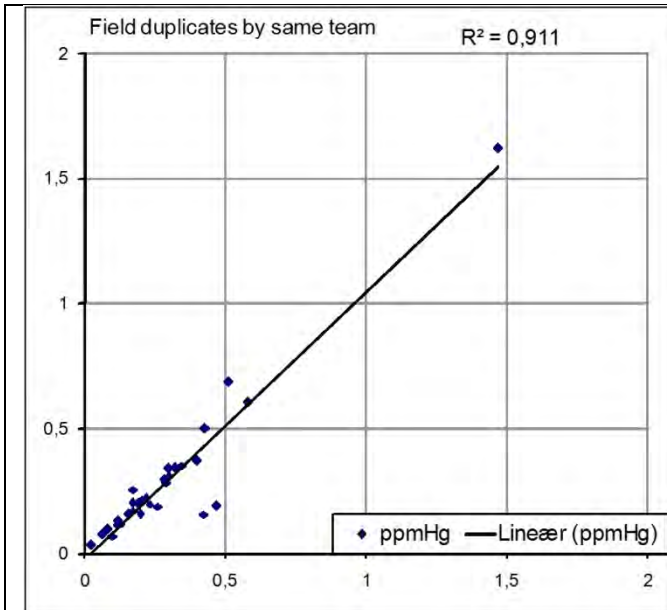


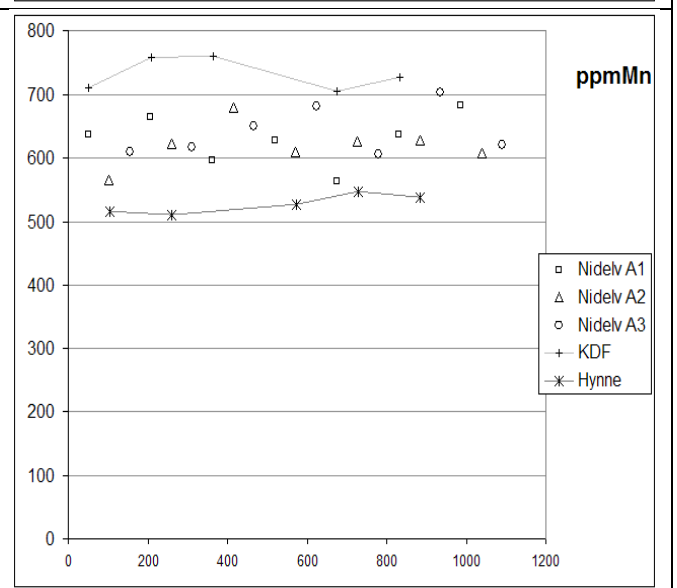
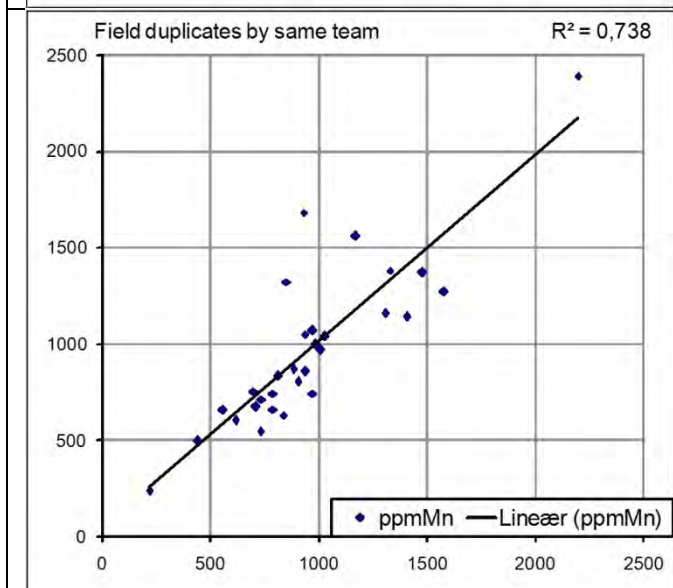
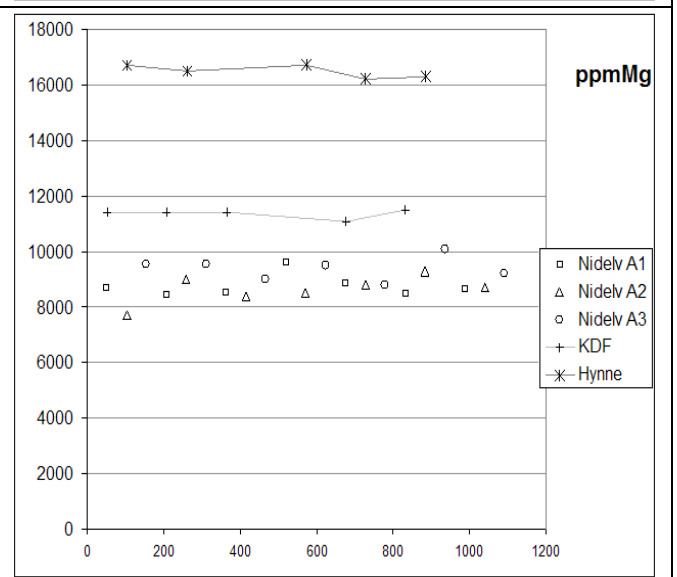
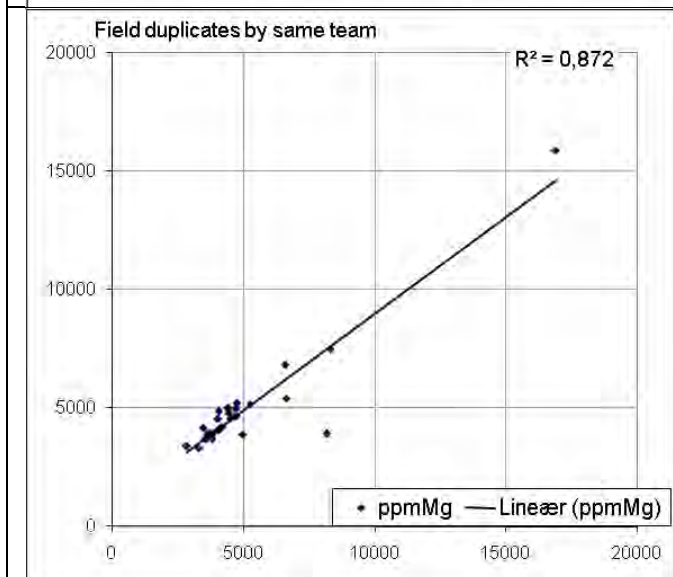
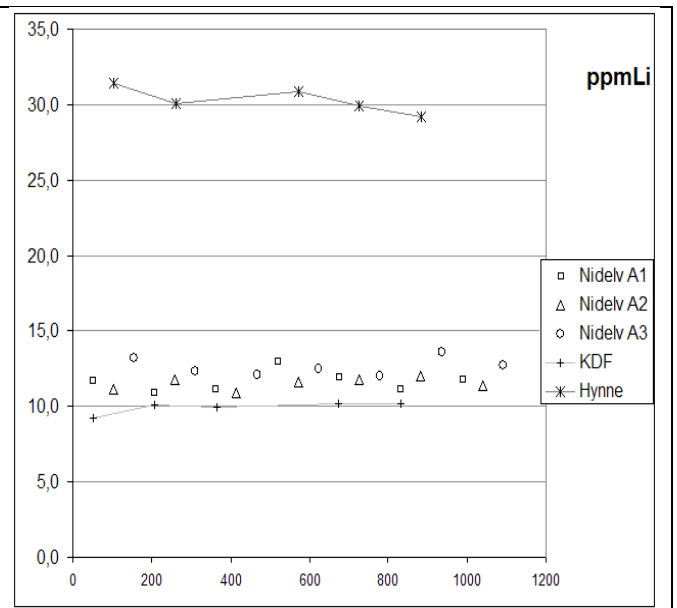
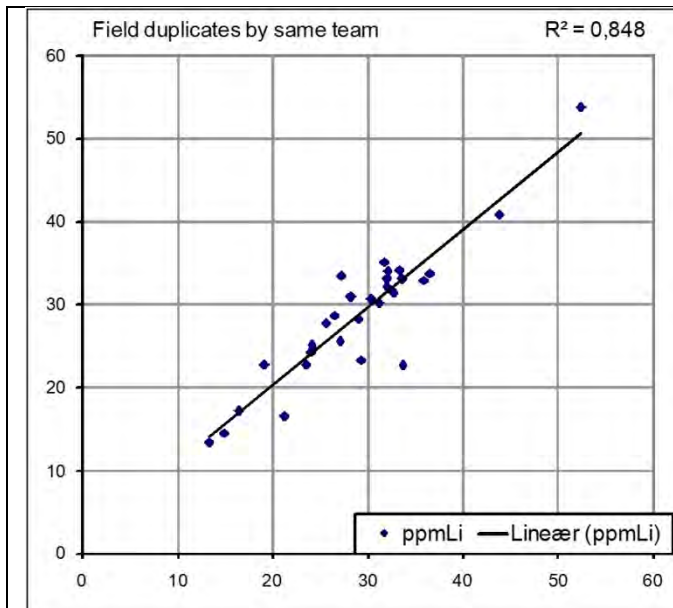


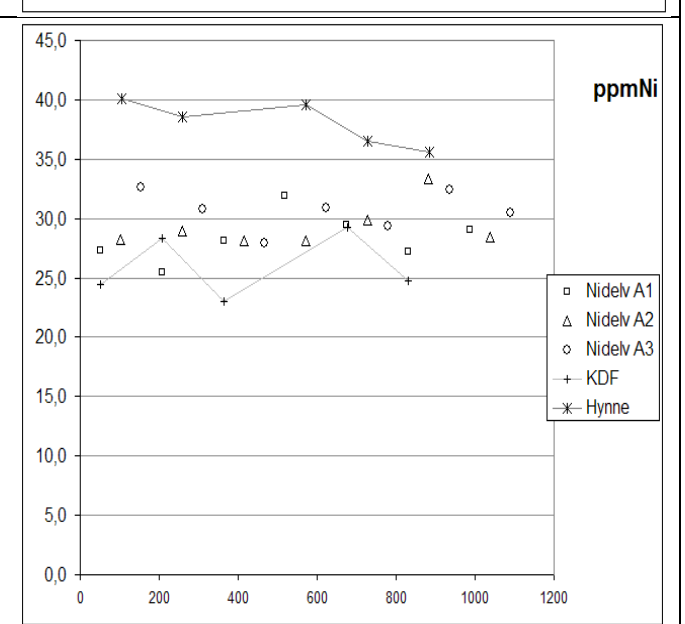
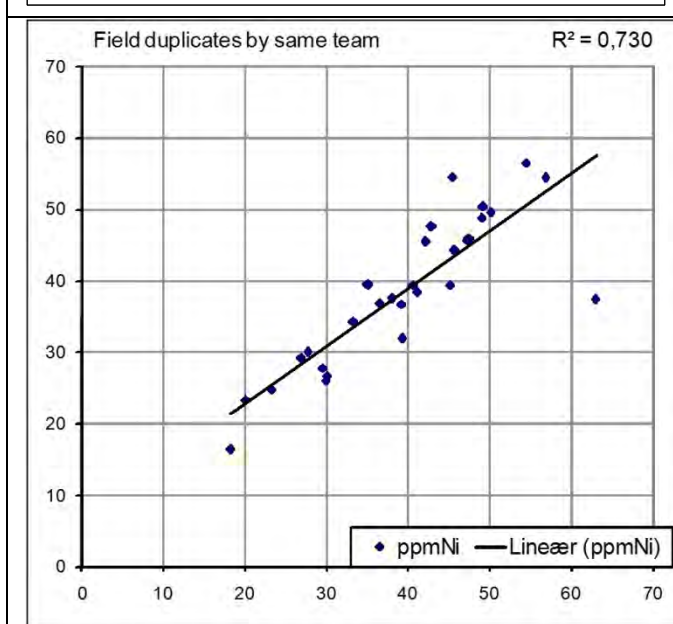
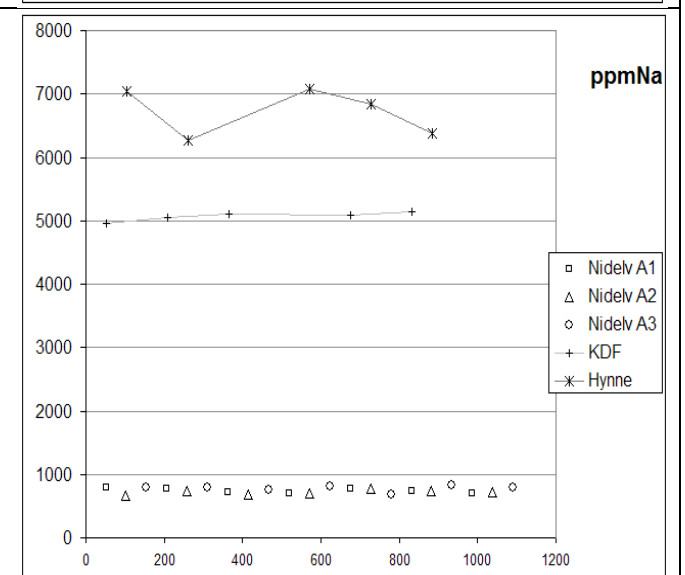
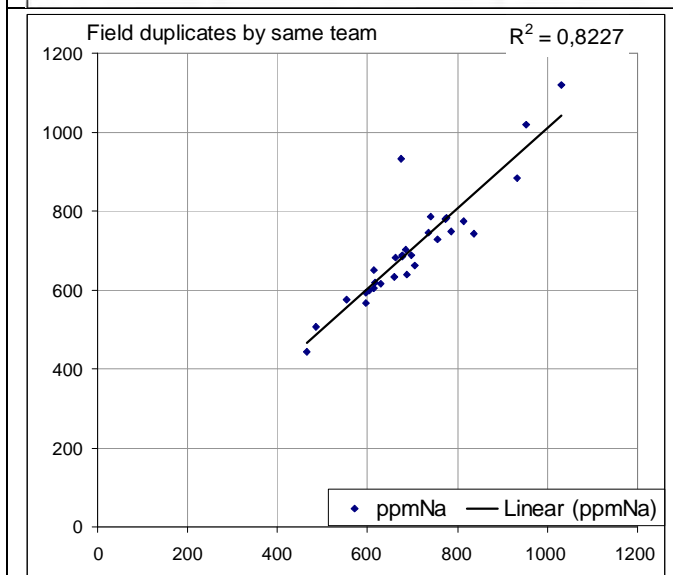
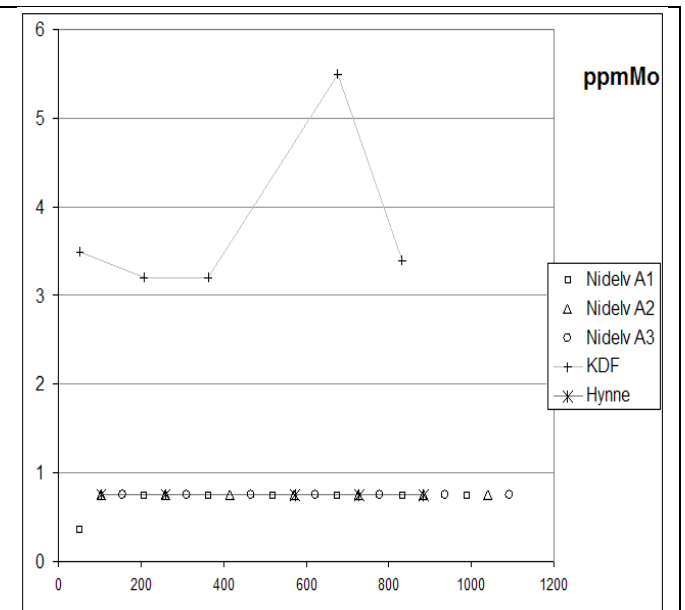
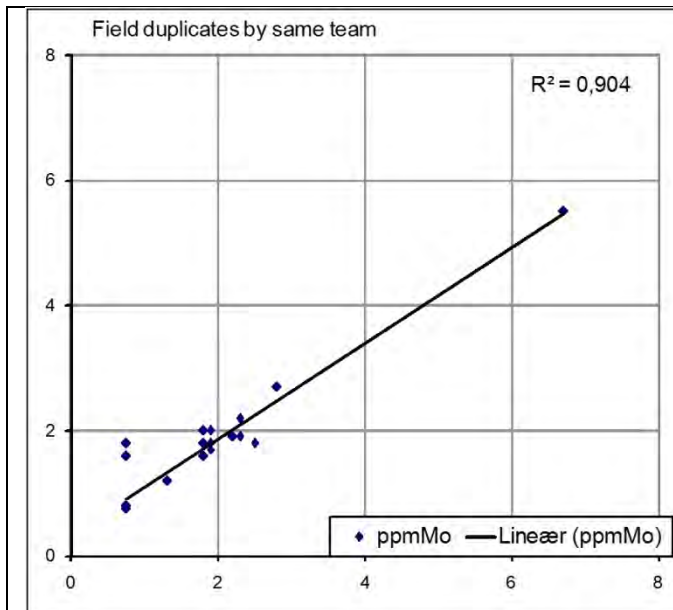


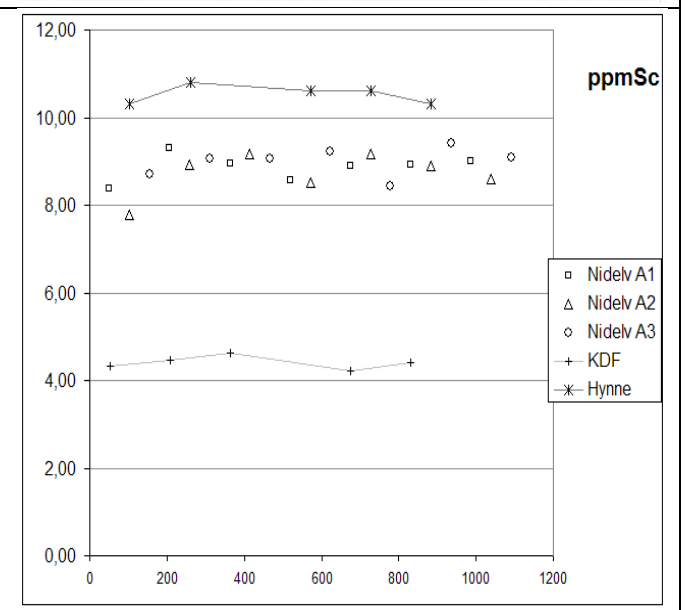
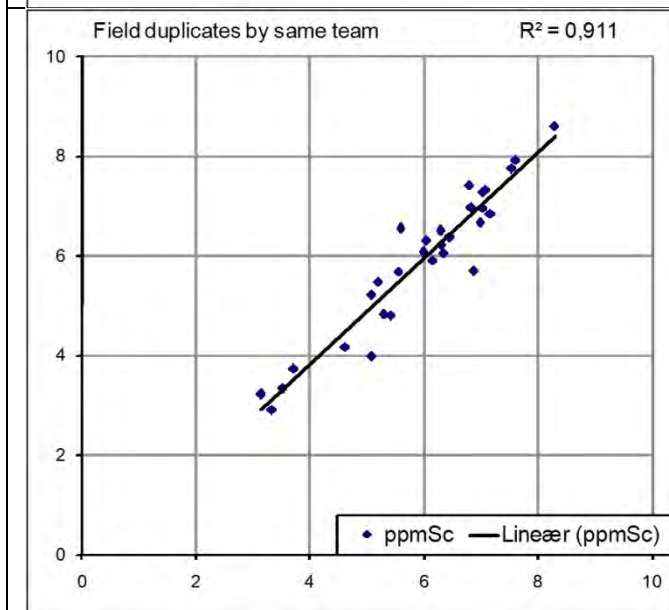
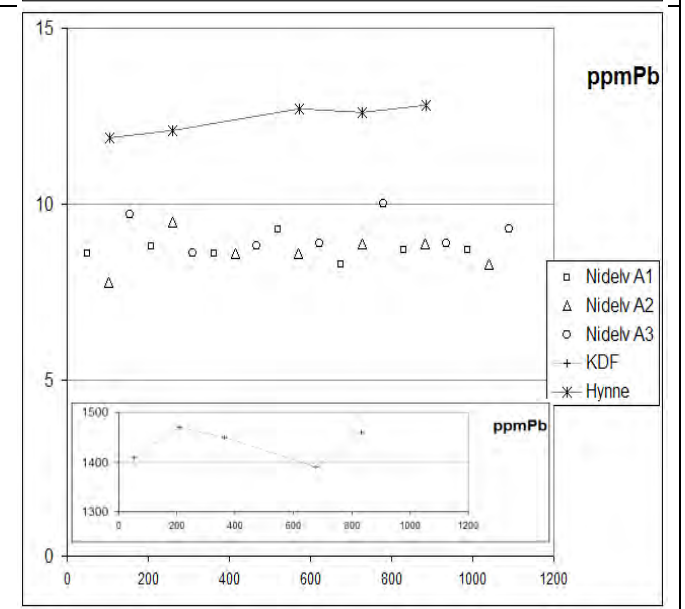
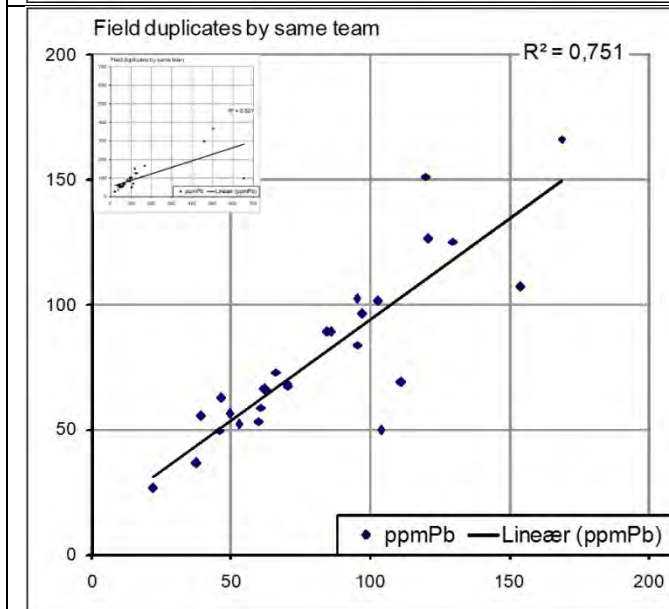
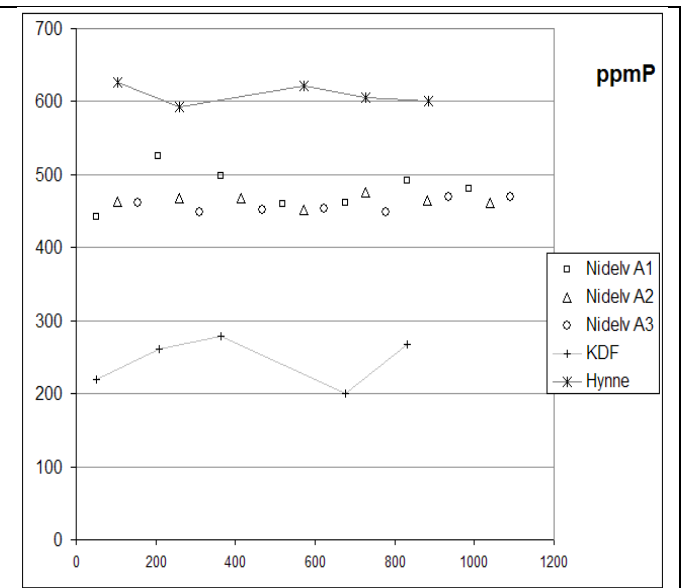
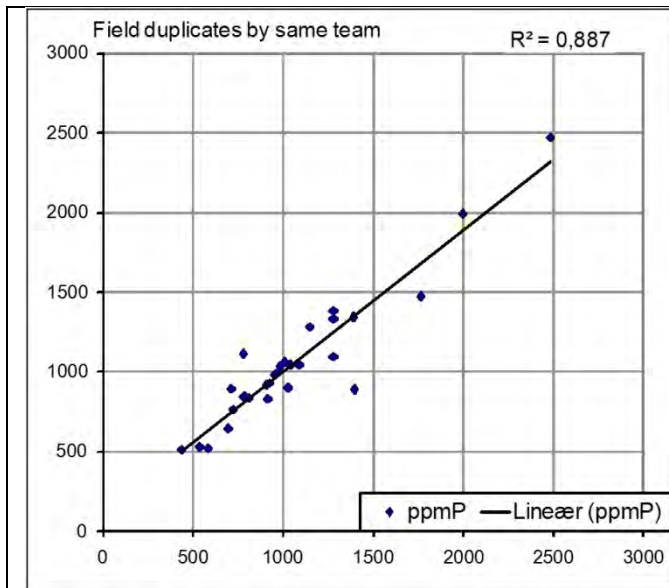




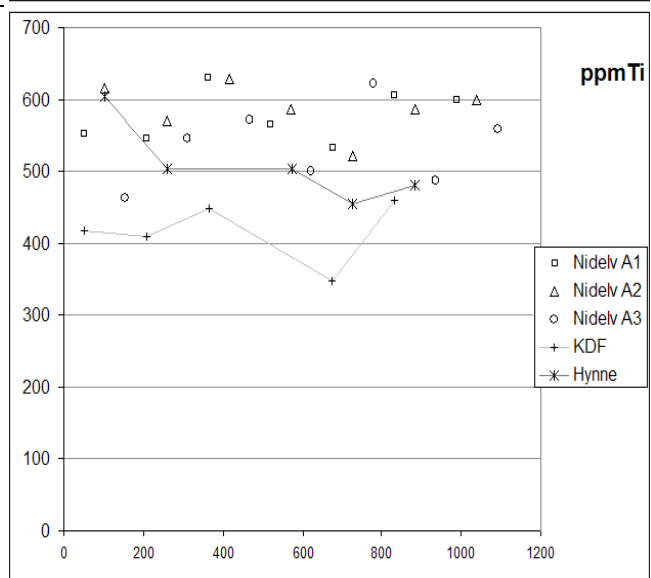
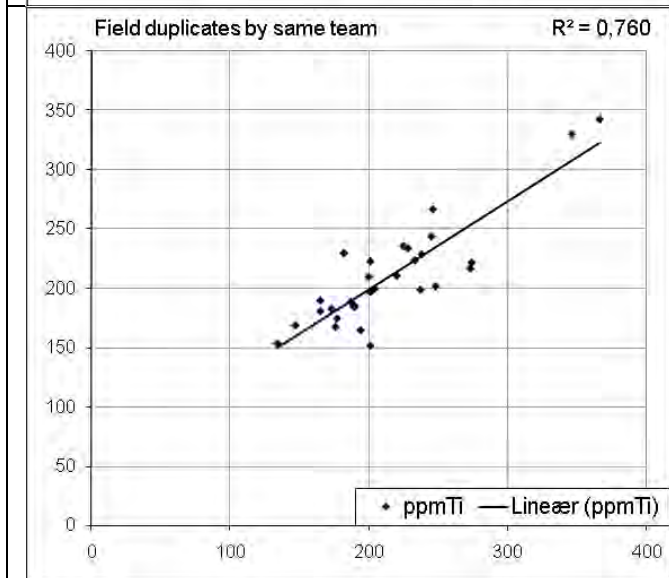
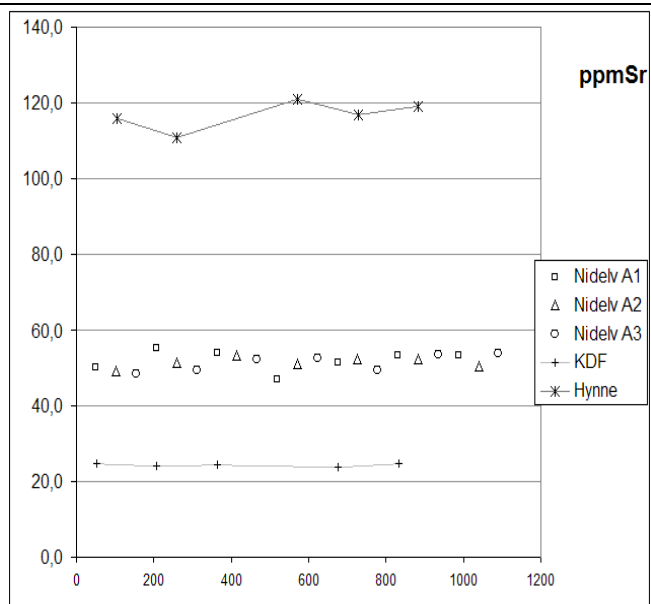
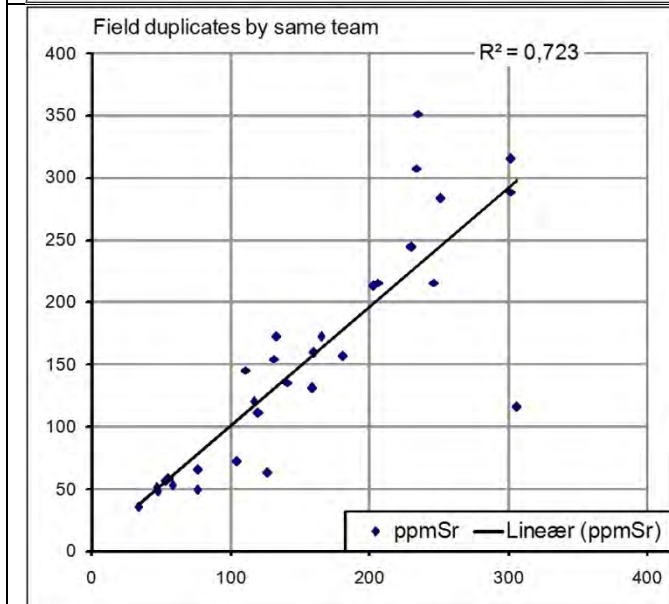
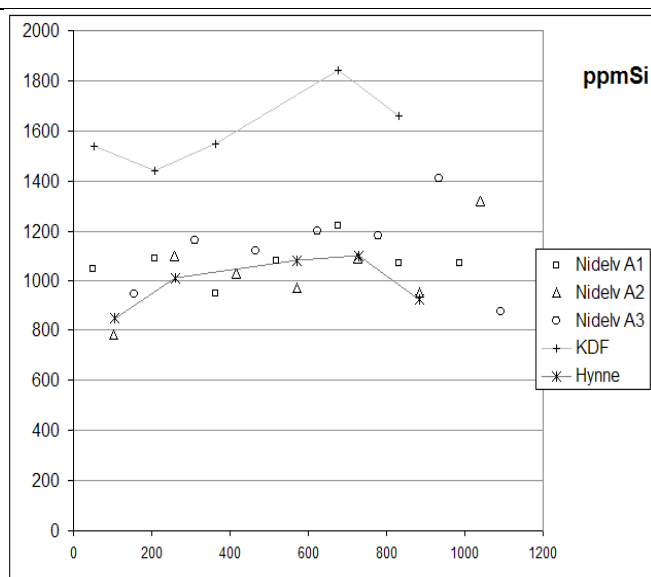
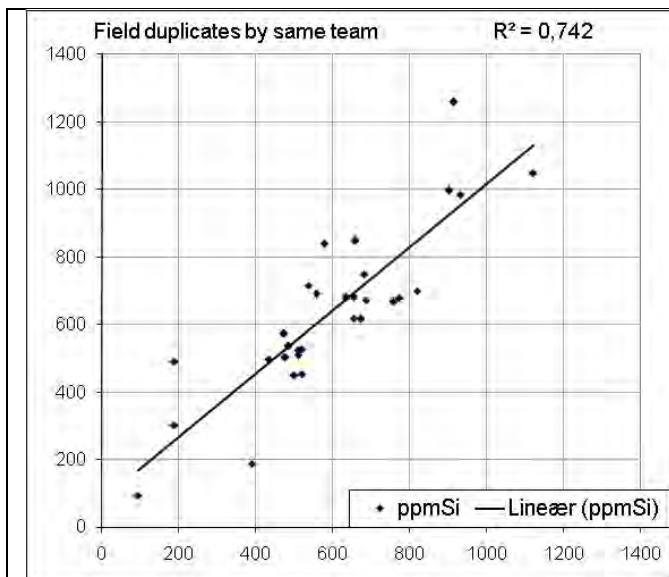


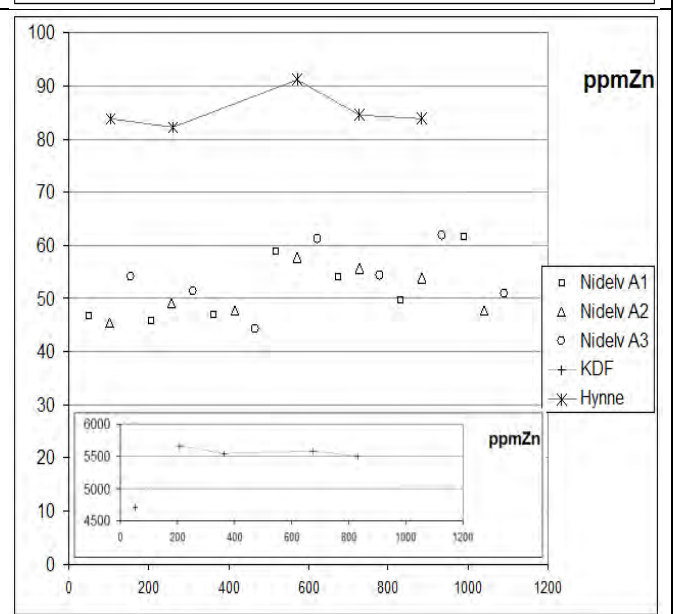
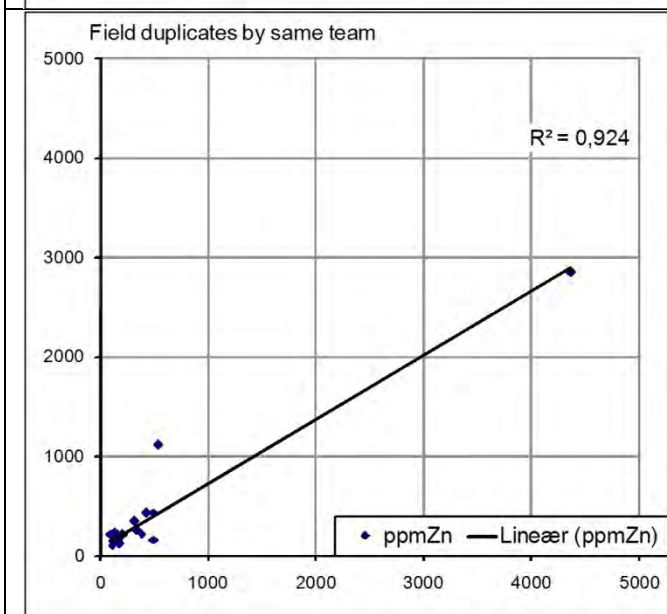
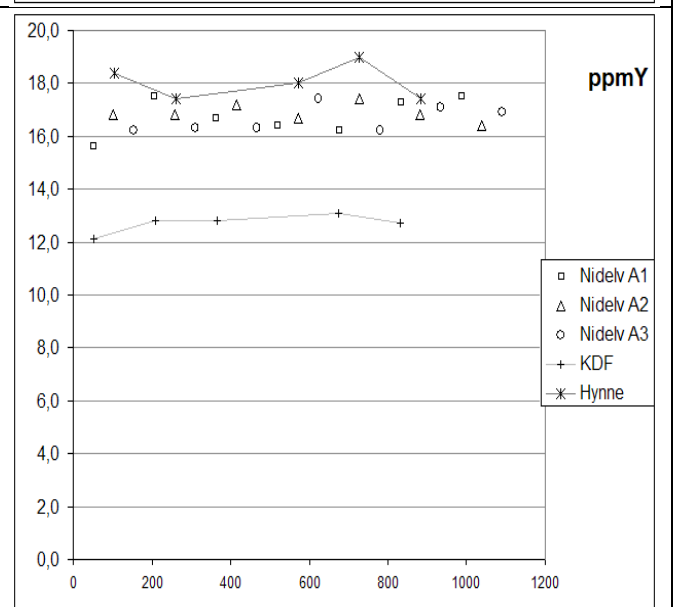
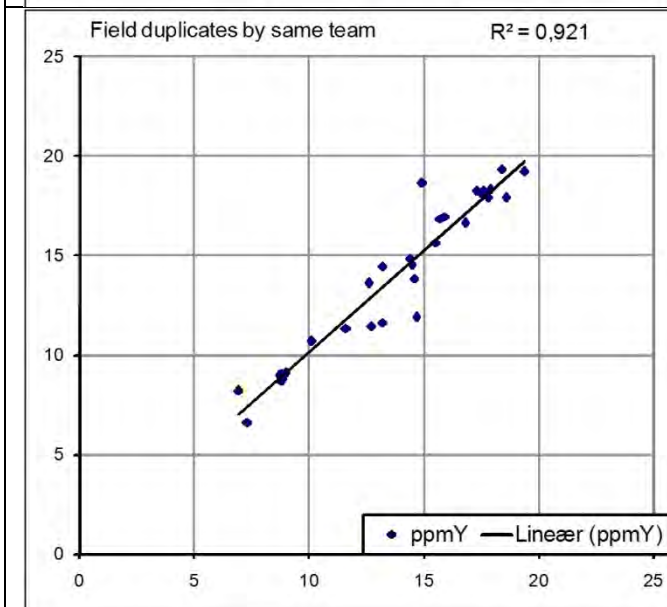
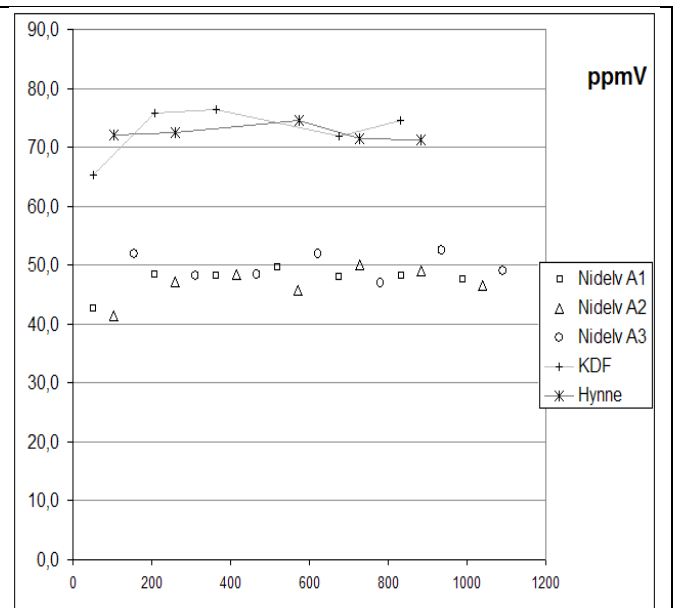
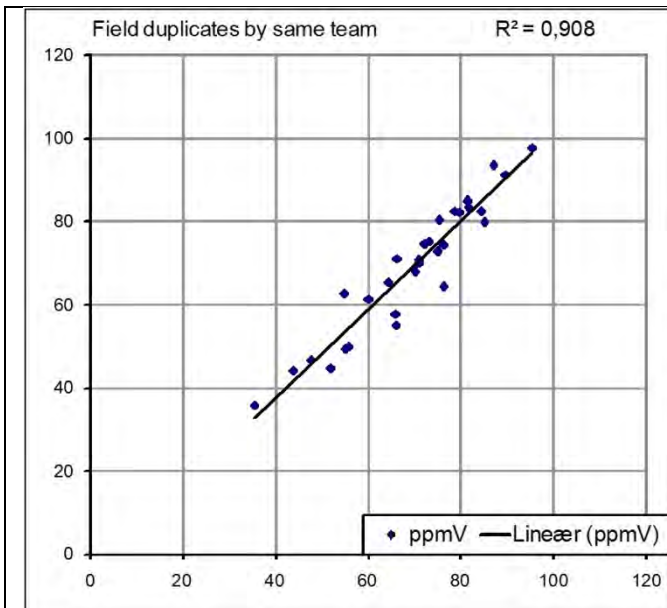


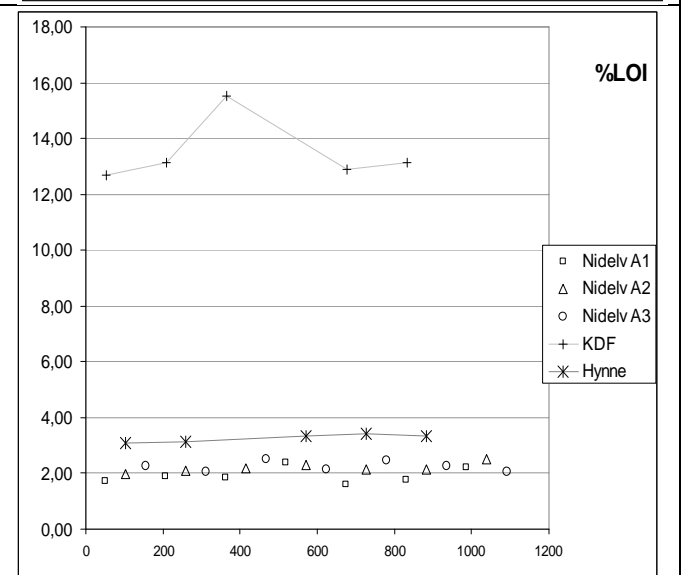
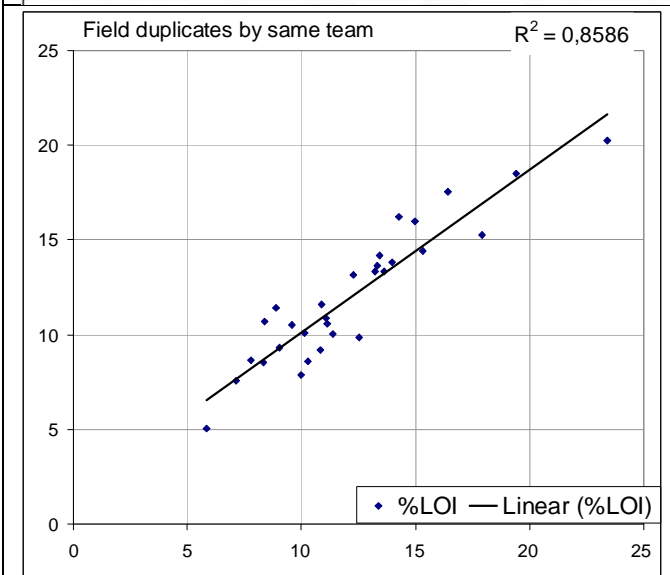
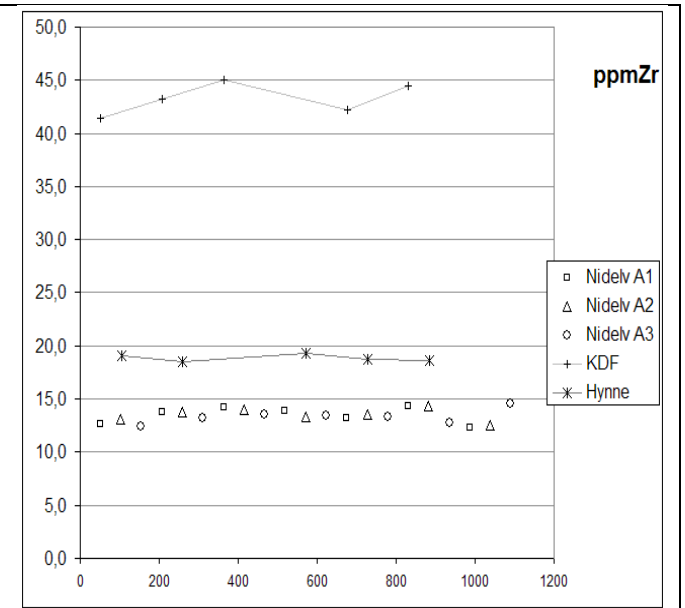
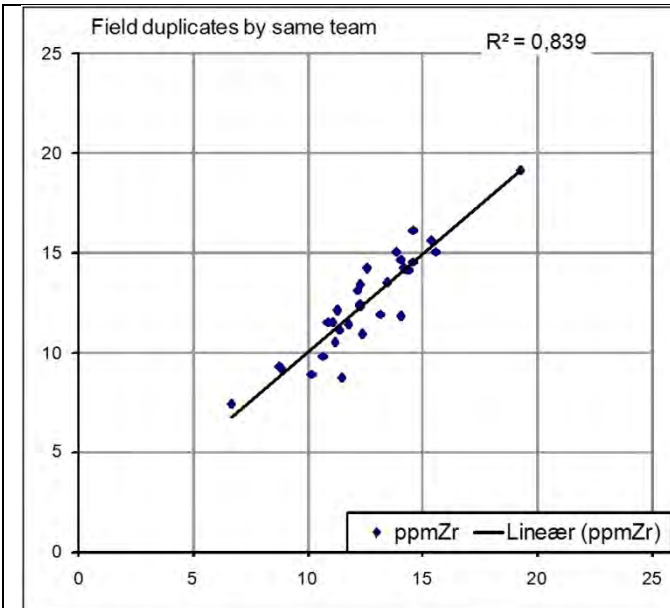












Summary of analytical data, control sample MESS-3 (NRC-CNRC). Certificate values are total content

Element	Mean	SD	%RSD	N	Median	Certificate	Rel. dev.%
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 %

Summary of analytical data, control sample NIST2709 (NIST). Certificate values are total content

Element	Mean	SD	%RSD	N	Median	Certificate	Rel. dev. %
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		

Field duplicates. X: Ordinary Y: Duplicate	STD samples. X: Sequence Y: Result
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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 %

Summary of analytical data, control sample SO2 (CCRMP, CANMET Mining and Mineral Sciences Laboratories). Certificate values are total content

Element	Mean	SD	%RSD	N	Median	Certificate	Rel. dev. %
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		