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Environmental impact statement

To support EU environmental policy-making for reducing the emissions and thus, the harmful impacts of heavy metals, monitoring programs are required in order to establish a coherent and comprehensive overview of the environmental quality status. In the latest report on the state of the European environment, the following key messages are given: "*A broader commitment to environmental monitoring and up-to-date reporting of environmental pollutants and wastes, using the best available information and technologies, will make environmental governance more effective*." Based on a regional case study, this paper summarizes the best available monitoring technology using ICP-MS for the determination of elements in our environment and the main hindrances for meeting the European environmental monitoring requirements.

Do ICP-MS based methods fulfill the EU monitoring requirements for the determination of elements in our environment ?

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Abstract

Undoubtedly, the most important advance in the environmental regulatory monitoring of elements of the last decade, is the widespread introduction of ICP-mass spectrometry (ICP-MS) under impulse of standards developed by the European Committee for Standardization. The versatility of ICP-MS units as a tool for the determination of major, minor and trace elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn, Ti, V and Zn) in surface water, groundwater, river sediment, topsoil, subsoil, fine particulates and atmospheric deposition is illustrated in this paper. Ranges of background concentrations for major, minor and trace elements obtained from a regional case study (Flanders, Belgium) are summarized for all of these environmental compartments and *discussed in the context of a harmonized implementation of European regulatory monitoring requirements. The results were derived from monitoring programs in support of EU environmental quality directives and were based on a selection of (non-polluted) background locations. Because of the availability of ICP-MS instruments nowadays, it can be argued that the main hindrance for meeting the European environmental monitoring requirements is no longer the technical feasibility of analysis at these concentration levels, but rather (i) potential contamination during sampling and analysis, (ii) too limited implementation of quality control programs, validating the routinely applied methods (including sampling and low level verification) and (iii) lack of harmonization in reporting of the chemical environmental status between the individual member states.*

Keywords: ICP-MS, ambient background concentrations, Flanders region, EU environmental quality directives, European Committee for Standardization

1 Introduction

The main aim of EU environmental directives (*i.e.*, the Water Framework Directive, the Air Quality Directive, the Waste Framework Directive and the upcoming Soil Framework Directive) is to create an environment in which the level of pollution does not give rise to harmful effects on human health and the environment [1,2,3].

The continuing presence of pollutants in Europe's freshwaters, their structural modifications and increasing problems with water scarcity and floods threatens aquatic ecosystems and raises concerns for public health. A substantial proportion of Europe's freshwaters did not achieve 'good status' by 2015, the initial goal of the EU Water Framework Directive (WFD) [4,5].

Emissions of air pollutants result from almost all economic and societal activities [6,7]. This results in clear risks to human health and the environment, *e.g.,* an estimated 5 million years of lost life per year are due to fine particles ($PM_{2.5}$) alone in the European economic area (32 countries) [6]. In Europe, policies and actions at all levels have significantly reduced anthropogenic emissions and exposure to important air pollutants such as sulphur dioxide and lead. However, complex links between emissions and ambient air quality mean that for some pollutants lower emissions have not produced a corresponding drop in the concentrations found in the environment.

In the latest report on the state of the European environment, the following key messages are given [6]: "*water and air pollution have declined, but not enough to achieve good ecological status in all water bodies or to ensure good air quality in all urban areas. A broader commitment to environmental monitoring and up-to-date reporting of environmental pollutants and wastes, using the best available information and technologies, will make environmental governance more effective*."

In all European directives related to environmental quality, "heavy metals" in the environment are of concern [1,2,3]. The term "heavy metals" is commonly used to address adverse effects of trace elements in our environment. Although IUPAC (International Union of Pure and Applied Chemistry, *i.e.*, the world authority on chemical nomenclature) explicitly criticised the use of the term "heavy metals" as ambiguous and pointless, this has not banned the term itself in both popular and scientific literature [8]. Today, the term "heavy metals" is simply defined as a set of elements frequently used in legislation without a widely accepted scientific rationale. Often, the elements of environmental concern are trace elements, which are defined by IUPAC as elements having an average concentration of less than 100 parts per million atoms (< 100 ppm).

To support EU environmental policy-making for reducing the emissions and thus, the harmful impacts of elements ("heavy metals"), monitoring programs are required in order to establish a coherent and comprehensive overview of the environmental quality status [1-3]. In order to assure equivalent scientific quality and comparability across Europe, methods standardised by the European Committee for Standardization (CEN), International Organization for Standardization (ISO) or national standardisation bodies are promoted to be used in the monitoring programs. However, the development of EN standards is governed by the principles of consensus and national commitment and this induces a lag in the use of best available instrumentation. To some extent, this can be circumvented by the use of Environmental Technology Verification (ETV), which has recently been introduced by the European Commission as a new tool to help innovative environmental technologies to reach the market [9].

For the determination of elements, sensitive instruments based on atomic spectrometry were commercially introduced as of the sixties of the last century. Atomic Absorption Spectrometry (AAS) became commercially available first, followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) in the seventies and inductively coupled plasma-mass spectrometry in the eighties (ICP-MS) [10,11]. In a 25-year retrospective spectrometry update published in 2010 it is stated that "*By far the most important advance in water analysis over the 25 year review period has been the development of ICP-MS from a research curiosity to a robust, precise and sensitive analytical tool that now can detect most elements in fresh and drinking waters without any sample pretreatment.*" [10]. However, the first EN standard (EN 17294-2:2004) related to ICP-MS was published in 2004 only, in contrast to the first United States Environmental Protection Agency (US EPA) standard (US EPA 200.8) related to ICP-MS for the determination of trace elements in water, which was already published in 1990 [12-17]. By now, European standard methods based on ICP-MS became available for the determination of trace elements in the different environmental compartments: air (EN 14902:2005), water (EN 17294-2:2004, EN 17294-1:2006) and soil (CEN/TS 16175-2:2013)[12-21].

Within the EU environmental directives, concentrations of heavy metals which should not be exceeded in order to protect human health and the environment are defined. The development of such environmental quality standards (EQS), include knowledge on natural background concentrations of elements [22]. The general definition of natural background level is the concentration that is present owing to natural and geological processes only, i.e. the background level without anthropogenic contribution ('pre-industrial' levels). In reality, true pristine areas are rare within Europe, and it must be considered on a case-by-case basis whether a given area represents a pristine condition for a specific element. In most areas in Europe, any estimate of a natural background concentration will inevitably include a small contribution from anthropogenic sources because much of Europe's landscape has been altered by man's activities for mineral extraction, agriculture or habitation for millennia and this historical contribution may be obscure [23-27]. In addition, long-term anthropogenic activities, such as drainage, irrigation and special crops (e.g., conifers creating acid soil conditions), may influence the environmental release of metals. This contribution is difficult to quantify and distinguish from what concentrations might have been in the absence of such activities. Finally, contributions from diffuse anthropogenic sources, e.g., atmospheric deposition, may be impossible to eliminate entirely. Therefore, any estimate of a background concentration will more likely be an 'ambient' background concentration rather than a value relating to a purely natural pristine environment. This holds especially true for the Flemish Region of Belgium, which is one of the most densely populated regions of Europe (450 persons per km² as compared to a European average of 105 persons per km²) and with an estimated fraction of paved surface (soil sealing) of 13 % (European average 1,8%)[28,29]. The heavy metal loads in Belgium are above the EU average loads, as shown by, *e.g.*, the relatively high emissions of Cd to air (7.8 ton/yr) due to oil combustion and Cd/CdO production, and input to agricultural soils through phosphate fertilizers and sludge [30]. Cd deposition rates (3.6 g/ha.yr) in rural areas are at the high end of the EU spectrum. Due to historical non-ferrous smelting activities starting at the end of the 19th century, an area of approximately 700 km² in the Campine region at the Dutch-Belgian border, is polluted with Cd and Zn. Moreover, the use of non-ferrous residues (zinc ash) for road stabilisation in more than 1300 km of roadways and more than 1000 driveways has also led to diffusely contaminated soil and groundwater in the Flemish Region [31].

In summary, ambient background concentrations are needed in support of environmental policy and as a case study, ranges of ambient background concentrations of elements were derived in this paper for the hydro-, litho- and atmosphere in Flanders (Belgium)[32]. For this purpose, samples from rural (non-polluted) background locations of surface water, groundwater, river sediment, topsoil, subsoil, fine particulates and atmospheric deposition were selected from (on-going) regulatory monitoring programs. All of the measurements were performed using ICP-MS based European standard methods. The primary focus and discussion of the paper is on the fit-for-purpose of ICP-MS methods for environmental monitoring on the one hand and on analytical issues in the context of a harmonized implementation of European regulatory monitoring requirements on the other.

2 Materials and methods

Environmental regulatory monitoring programs in support of EU environmental policy-making are performed in the Flanders region of Belgium under the responsibility of different Environmental Agencies. In order to establish a coherent overview of ambient background concentrations, only samples collected at rural background locations of surface water, groundwater, river sediment, topsoil, subsoil, fine particulates and atmospheric deposition were selected from these (on-going) monitoring programs. In the following paragraphs and per environmental compartment, the selection of the samples as well as the ICP-MS based European standard monitoring methods are described.

2.1 Ambient background concentration of elements in soil

For the determination of ambient background concentrations of elements in soil, 45 topsoil samples (0-20 cm and 50-100 cm) and 45 subsoil samples (tertiary deposits, depth range 4-500 m, median: 76 m) were collected in Flanders in 2006 [32,33]. The locations were selected based on the absence of anthropogenic influence and on being representative for the variation of soil textures in Flanders (see Figure 1). The method used for the determination of elements in soil was based on CEN/TS 16171:2012 [21]. In short, the procedure involved drying, sieving of the soil sample with a 2 mm sieve and milling. Subsequently, about 0.5 g of the sample was weighed in a digestion vessel; 6 ml of 12 M HCl and 2 ml of 16 M HNO_3 (*aqua regia*) were added and the sample was digested in a microwave system. The temperature of the digestion mixture in each vessel was raised to and remained at 175°C for 10 min. The digest thus obtained was transferred to a volumetric flask of 100 ml and made up to volume. Prior to ICP-MS analysis, that digest was diluted 5-fold with Milli-Q water.

2.2 Ambient background concentration of elements in fine particulates

Particles with an aerodynamic diameter less than 10 µm (PM_{10}) were sampled once a week during the period 2008-2010, at ambient background locations in Flanders (Moerkerke, Aarschot and Retie, see Figure 1)[32]. PM_{10} sampling was performed by sampling of 55 m³ air through a quartz filter (Ø 47mm) over a period of 24 hours. In total, 250 quartz filter samples were collected during this campaign. On return to the lab, the filters were weighed to determine the total amount of PM_{10} collected. Subsequently, the filter was analysed for elemental composition according to EN 14902:2005 [19]. The filter was transferred into a microwave digestion vessel, 8 ml of 16 M HNO_3 and 2 ml of 10 M H_2O_2 were added, while ensuring complete submersion of the filter in the acid mixture. The microwave was programmed so that the acid mixture reached approximately 180 °C within 20 min. Subsequently, the temperature was slowly increased to up to approximately 220 °C and then held at that temperature for about 20 min. After the digestion procedure, the vessels were allowed to cool down to room temperature. The digestion solutions were transferred into volumetric flasks of 100 ml and diluted to the mark with ultrapure water.

2.3 Ambient background concentration of elements in atmospheric deposition

Total atmospheric deposition of elements for ambient background concentration was estimated with wet-only collectors at Koksijde on a weekly basis and with bulk collectors at Koksijde and Bonheiden on a monthly basis (see Figure 1))[32]. The wet-only collector is designed to collect only sedimenting wet particles, while the bulk collector is designed to collect all sedimenting – wet and dry – particles. For assessment of the wet deposition of Hg, samples were taken on a weekly basis at Koksijde and background concentrations of total gaseous Hg were continuously monitored with an automated mercury analyser at Houtem (Veurne). The methods used for the determination of elements in atmospheric deposition were based on EN 15841:2009, EN 15853:2010 and EN 15852:2010 [20,34,35]. EN 15841 specifies methods for sampling wet-only and bulk deposition of As, Cd, Ni and Pb. The samples of the bulk and wet-only collectors were transferred to the laboratory in the sampling bottle and acidified with nitric acid (to 1 v/v %). A 50 ml test portion of each sample was subsequently microwave-digested after adding a suitable volume of HNO_3 (*i.e.*, 2 ml) and analysed by ICP-MS.

2.4 Ambient background concentration of elements in river sediment

Since 2000, the Flemish Environmental Agency is monitoring the sediment quality at 600 locations in Flanders in both navigable and unnavigable waters, according to the Triad approach. This Triad sediment quality assessment is an integrated investigation technique based on the analysis of physico-chemical, biological and ecotoxicological parameters [36]. For the determination of median ambient background concentrations of elements, only those locations with no acute impact on benthic biota (= best ecotoxicological class) and good biological quality (= presence of benthic macro invertebrates, best biological class) were selected)[32]. From the 228 river sediment locations sampled during the 2010-2011 monitoring campaign, the selection criteria were met at 22 locations (only these locations are indicated in Figure 1). The methods used for the determination of elements in river sediment were based on EN 16174:2012, CEN/TS 16171:2012 and EPA 7473:1998 [21,37,38].

2.5 Ambient background concentration of dissolved elements in surface water

The Flemish Environment Agency started the monitoring of dissolved elements in 2007 and systematically expanded the monitoring network to about 500 measuring points at present. For the determination of median ambient background concentrations of dissolved trace elements in Flemish surface water, the same 22 background locations (exhibiting no acute impact on benthic biota and with good biological quality) were chosen as for river sediment)[32]. The method used for the determination of dissolved elements in surface water was based on EN 17294-2:2004 [12].

2.6 Ambient background concentration of dissolved elements in groundwater

The Flanders Subsoil Database includes 2 major groundwater monitoring networks (primary and phreatic) with the intention of getting a representative picture of the groundwater quantity and quality of the aquifers in Flanders [39]. In the context of environmental monitoring, the phreatic groundwater monitoring network and the primary groundwater monitoring network are of importance. The phreatic groundwater monitoring network was originally established as a monitoring tool in function of the European Nitrate Directive (91/676/EEC). On a half-yearly basis, 2107 multi-level wells (with about 5100 filter screens) in agricultural areas and approximately 80 multi-level wells (190 filter screens) in natural areas were sampled and analysed. The primary monitoring network consists of about 435 wells with more than 800 screens, selected to provide representative data of important, mainly deeper, aquifers. The primary groundwater monitoring network aims primarily at establishing the regional groundwater reserves and at following the evolution of the quantity of the groundwater bodies in time. For the determination of ambient background levels of dissolved elements in the 42 groundwater bodies defined in Flanders, data from the primary and the phreatic groundwater monitoring network of 2006 were used)[32]. The method used for the determination of dissolved elements in surface water was based on EN 17294-2:2004 [12].

2.7 Statistics

Box-and-whisker plots were used for visualizing the background concentration ranges that were determined in the different monitoring studies. Box-and-whisker plots display differences between populations without making any assumptions on the underlying statistical distribution: they are non-parametric. The median/quartile/range type of plots were computed using Statistica (StatSoft, Inc. (2011), STATISTICA (data analysis software system), version 10. www.statsoft.com). The spread (variability) in the values is represented by the quartiles (the 25th and 75th percentiles, height = H) and the non-outlier range (the "whiskers" in the plot). The non-outlier range is the range of values that fall below the upper outlier limit (*i.e.*, + 1.5 * the height of the box, H) and above the lower outlier limit (*i.e.*, -1.5 * the height of the box, H). The upper value of the box in the box plot (*i.e.*, the 75th percentile) is indicated as UBV, the lower value of the box in the box plot (*i.e.*, the 25th percentile) is indicated as LBV. A data point is considered to be an outlier value if the following conditions hold : data point value > UBV + 1,5*(UBV - LBV) or data point value < LBV – 1,5*(UBV – LBV). A data point is considered to be an extreme value if the following conditions hold: data point value > UBV + 3 *(UBV - LBV) or data point value < LBV – 3 *(UBV - LBV).

3 Results and discussion

In the following paragraphs, an inventory of regulatory monitoring studies that have been performed in Flanders (Belgium) is discussed with special attention to the derivation of ambient background concentrations of elements. The median background concentration of elements for the hydro-, litho- and atmosphere summarised in Table 1 can be considered as an estimate of the current "natural" chemical status of the Flemish environment and can be used to assess future anthropogenic influences within an EU regulatory monitoring context.

The primary focus and discussion of the paper is on the fit-for-purpose of ICP-MS methods for environmental monitoring on the one hand and on analytical issues in the context of a harmonized implementation of European regulatory monitoring requirements on the other. Therefore, performance characteristics of the ICP-MS standard monitoring methods used for the determination of elements in the different environmental compartments are summarised and discussed. The most commonly used type of mass spectrometer in ICP-MS instrumentation nowadays is the quadrupole mass filter (ICP-QMS), however other type of mass spectrometers, *e.g.*, a double-focusing sector field mass spectrometer (ICP-SFMS) or a time-of-flight analyser (ICP-TOFMS) are used in commercially available instrument types as well. Dealing with spectral interferences when analysing environmental samples is the Achilles' heel of the ICP-MS methods. Among all approaches for overcoming spectral overlap, those based on instrumental improvements have been most successful and in particular, the application of collision/reaction cells in front of a low resolution quadrupole mass analyser has significantly extended the spectrum of applications in ICP-QMS. As a consequence, this type of instrument is nowadays used in all (major) ISO 17025 accredited environmental laboratories operating in the Flanders Region [40].

3.1 Ambient background concentration of elements in soil

In anticipation of a European Soil Framework Directive with the objective to protect soils across the EU, the Flemish Government pioneered in 1996 with the first Soil Remediation and Protection Decree (VLAREBO, 1996)[13]. In this context, soil quality reference values were needed to be developed as a basis to identify and assess soil contamination processes at regional level. Hence, there was a need to establish levels of trace elements currently found in common (clean) soils. Elemental ambient background concentrations in 45 topsoil samples (0-20 cm and 50-100 cm) and 45 subsoil samples (Tertiary soils) collected at different locations are summarised in Figure 2.

3.1.1 Performance characteristics of ICP-MS method (CEN/TS 16171)

Limits of detection (LoDs) of the ICP-MS reported method were in the order of 10 – 50 µg kg^{-1} soil (calculated as 3 x st. dev. on 10 procedure blank solution analyses). The trueness of the method was determined by analysing certified reference material BCR-141R (Trace elements in calcareous loam soil), BCR-144R (Sewage Sludge) and BCR-146R (Sewage sludge). The recovery for the certified elements (Cd, Co, Cr, Cu, Ni, Pb and Zn) ranged between 94 and 103 %, which is in line with other reported ICP-MS data on these reference materials [41]. The precision expressed as 95 % confidence interval is dependent on the concentration level in soil analysis. According to multiple soil analyses within the context of validation of CEN/TS 16171, a median precision of 7 % in the range > 10 mg kg^{-1}, 12 % in the range 1-10 mg kg^{-1} and 18 % in the range < 1 mg/kg was derived [42].

3.1.2 Harmonized implementation of European regulatory monitoring requirements

The choice of the acid digestion procedure has an effect on the accuracy and precision attainable in the multi-elemental analysis of soil [16]. In the Flanders region of Belgium, the same acid digestion procedure (EN 13656, including the use of fluoric acid, HF) is used for the determination of elements in soil and waste [15]. In most European countries, *aqua regia* (HCl/HNO_3) or nitric acid digestion is performed for the subsequent determination of elements in soil. In the case of *aqua regia* digestion (CEN/TS 16171), complete solubilisation of refractory minerals is not achieved. This is illustrated for the determination of Cr in soils in Figure 3. Only, *ca*. 80 % of the total Cr amount is recovered from soil using *aqua regia* digestion as compared to the recovery achieved with the acid digestion procedure with the supplementary use of HF.

When defining a background value for any one element in future European soil legislation, it is important to consider that the occurrence of ore deposits and geology play the key role in determining the element distribution patterns. This was also noticed in the GEMAS (Geochemical Mapping of Agricultural Soils of Europe) project [43,44]. In order to provide harmonised geochemical data of arable land and land under permanent grass cover at the European scale (requirements of the REACH regulation), a geological survey was performed in 34 European countries, covering an area of approximately 5.6 million km^2 at a sample density of 1 site per 2500 km^2, collecting one sample from arable land (0–20 cm) and land under permanent grass cover (0–10 cm), each [43-45]. Soil samples were digested via HNO_3/HCl digestion and analysed by ICP-MS. On average, there is a factor of 6 difference among the median concentrations of the elements reported by the countries involved in the study. Several elements (*e.g.*, Ni) even show a substantially larger difference up to a factor of more than 100. For comparison, in the 45 topsoil samples analysed in our regional case study, there was, on average, a factor of 7 difference in the concentration per element (factor calculated as the ratio $90^{th}/10^{th}$ percentile) and an average difference factor of 15 in the concentration per element for the 45 subsoil samples.

3.2 Ambient background concentration of elements in fine particulates

The issue of air quality is still a major concern for many European citizens. Fine particulates (PM_{10}, particles with an aerodynamic diameter less than 10 μm) present a health risk which is of increasing concern in Flanders. It is therefore important to identify the sources and causes of this type of pollution. To do so, the Flemish Environment Agency (VMM) has carried out several particulate matter (PM) chemical characterisation studies, where hot spots and rural background sites were monitored [46-48]. For the derivation of ambient background concentration of elements in PM_{10} in Flanders, 3 different background locations from the PM chemical characterization studies were selected. The results of the analysis of 250 PM_{10} samples collected at these locations are summarised in Figure 4.

3.2.1 Performance characteristics of ICP-MS method (EN 14902)

LoDs of the reported ICP-MS method, calculated as 3 x st. dev. on 24 procedure blank solution analyses were in the order of 5 – 50 ng/filter (corresponding to ~ 0.01 to 0.1 ng m^{-3}) for Ag, As, Cd, Co, Cr, Mn, Mo, Ni, Sb, Sn, Tl, V and 50-500 ng/filter (corresponding to ~ 0.1 to 1 ng m^{-3}) for Ba, Cu, Fe, Pb, Se, Zn and 5000 ng/filter (corresponding to ~ 10 ng m^{-3}) for Al [49]. These instrumental LoDs cover possible contamination during the acid digestion procedure and instrumental power of detection. In order to verify the possible contribution of the type of filter, 10 blank Polytetrafluoroethylene (PTFE) and 10 blank quartz filters were digested and analysed. When using PTFE filters, no significant contribution was observed. However, when using quartz filters, a filter material background concentration was observed for Ni (30 ng/filter), Mn (60 ng/filter), Cr (130 ng/filter), Zn (700 ng/filter), Ba (1200 ng/filter) and Fe (1900 ng/filter). The trueness of procedure EN 14902 was controlled by checking the recovery of elements from NIST SRM 2584 (Trace Elements in Indoor Dust). EN 14902 stipulates that the average recovery for Cd and Pb should be between 90-110 % and for As and Ni between 85-115%. These requirements were fulfilled for the average recovery obtained upon 30 analyses of NIST SRM 2854 for As (100%), Cd (98%), and Pb (93%), but not for Ni (66%). The value for Ni in NIST SRM 2854 is an indicative value (not a certified one), however the average recovery of Cr also amounts to 72% only (see also Figure 3 related to soil analysis), indicating that refractory elements may not completely solubilise using the HNO_3/H_2O_2 digestion and that the supplementary use of, *e.g.*, HF for complete recovery of Ni from PM_{10} is needed [50]. The average recovery for other elements with indicative values amounted to: Ba (87 %), Co (87%), Cu (92%), Mn (83%), Mo (80%), Sb (29%), Se (102%), V (80%) and Zn (99%). For comparison purposes, NIST SRM 2854 was also microwave-assisted acid-digested using HNO_3 and HF and the digest thus obtained analysed via ICP-AES according to EN 14385 [51]. This European Standard specifies a reference method for the determination of the mass concentration of specific elements in exhaust gases from hazardous and municipal waste incinerators. The recovery for all elements was in the range 90-110 %, underlining the influence of the acids used in the digestion procedure. The precision expressed as 95 % confidence interval on PM_{10} is dependent on the concentration level. Based on multiple analysis of NIST SRM 2854 (n=30) according to EN 14902, a precision in the range of 10 to 20 % was derived for all elements, with the exception of Sb (32%). These results are in line with reported performance characteristics of method EN 14902 based on an European interlaboratory comparison exercise [52].

3.2.2 Harmonized implementation of European regulatory monitoring requirements

For the determination of ambient background concentrations of elements, the power of detection of ICP-MS is needed, especially for the determination of Cd. LoDs attainable with alternative methods as energy-dispersive and Wavelength-dispersive X-ray fluorescence (EDXRF and WDXRF, respectively) are in the order of 150 and 50 ng Cd/filter, respectively [53,54]. This corresponds to ~ 1 ng m^{-3} (WDXRF) and is a factor of 10 higher than the LoD obtained according to method EN 14902 using ICP-MS (and well above the median background value of 0.2 ng m^{-3} Cd). For the determination of the other elements for which European Air quality limits have been defined so far (As, Ni and Pb), the power of detection of EN 14902 using ICP-MS or EDXRF are both fit for purpose. However, in analogy to soil digestion, the HNO_3/H_2O_2 digestion (EN 14902) may not completely solubilise refractory elements, *e.g.*, Ni, and the use of HF for complete recovery from PM_{10} may be needed.

According to the Air quality in Europe report 2011, based on information reported by the individual European member states, the annual mean concentrations of Cd in PM_{10} in Belgium at different locations seem elevated (> 5 ng m^{-3}) in comparison with that in other European member states (< 2 ng m^{-3}) [55]. However it must be noted that the monitoring stations in the Flemish region are a mix of traffic, industrial and rural or urban background areas. Differences in locations of the monitoring stations between member states are of concern and interpretation or comparison of the chemical status should therefore be done carefully.

3.3 Ambient background concentration of elements in atmospheric deposition

Total atmospheric deposition of elements, which is defined as the sum of wet and dry deposition, can be estimated using wet-only and bulk collectors. The wet-only collector is designed to collect only sedimenting wet particles, while the bulk collector is designed to collect all sedimenting, wet and dry, particles. Ambient background concentration of elements in total atmospheric deposition and in wet atmospheric deposition are summarised in Figure 5 and Figure 6, respectively.

3.3.1 Performance characteristics of ICP-MS method (EN 15841)

LoDs calculated as 3 x st. dev. on replicate ICP-MS measurements of blank collectors are reported in the order of 0.05 – 0.2 µg m^{-2}.day^{-1}. For Hg, weekly measurements in wet deposition sampled at Koksijde were carried out with Cold Vapour Atomic Fluorescence Spectroscopy (CV-AFS) according to EN 15853. The CV-AFS method LoD is 0.001 µg m^{-2}.day^{-1} with a precision (95 % confidence interval) of less than 10 %. Based on duplicate sampling, a combined uncertainty (ca. 95% confidence level) of 53 % was derived for the Hg monitoring method [56].

3.3.2 Harmonized implementation of European regulatory monitoring requirements

Especially for Cd and As, the superior power of detection of ICP-MS is needed for ambient background determination in atmospheric deposition. Based on duplicate sampling of bulk depositions at Koksijde, a precision (95 % confidence interval) of better than 20 % is achieved for all elements in 80 % of the depositions monitored. However, in the other cases, a difference of up to a factor of 4 was observed between the duplicate measurements, illustrating that contamination (*e.g.*, Cu, Zn) may represent a far greater challenge than adequate instrumental LoDs for regulatory environmental monitoring. Lack of cleaning of air sampler equipment is often overlooked as a potential source of contamination in trace air analysis.

3.4 Ambient background concentration of elements in river sediment

The sediment quality is monitored at 600 locations in Flanders in both navigable and unnavigable waters, according to the Triad approach (analysis of physico-chemical, biological and ecotoxicological parameters)[36]. For the evaluation of the physico-chemical parameters, a standardisation to an organic matter content of 5% and a clay content of 11% is done for “heavy metals” and organic contaminants.

Ambient background concentrations of elements (reported as such, without standardisation to clay/organic matter) in river sediment collected at 22 different locations in Flanders (see Figure 1) and determined with ICP-MS after *aqua regia* digestion according to CEN/TS 16171 are summarised in Figure 7.

3.4.1 Performance characteristics of ICP-MS method (CEN/TS 16171)

The trueness of procedure CEN/TS 16171 was evaluated by the addition of spikes. The average recovery for these spikes varied between 90-110 %. The precision of procedure CEN/TS 16171 (*aqua regia* digestion) on river sediments, expressed as 95 % confidence interval, is dependent on the concentration level and in the range of 14-24 % for all elements.

3.4.2 Harmonized implementation of European regulatory monitoring requirements

For the elements Cd and Se, the superior power of detection of ICP-MS, as compared to ICP-AES, is necessary to determine background concentrations. An advantage of ICP-MS is that in addition to trace elements at mg/kg level, also matrix elements at g/kg level can be determined in the same measurement run (panoramic analysis)[57]. Besides organic matter and clay content, also the total Fe and Ca contents are relevant parameters to predict elemental concentrations in sediments, [58]. The results for these matrix elements at the 22 background locations selected are summarised in Figure 8.

3.5 Ambient background concentration of elements in surface water

Surface waters at 22 selected background locations were sampled and analysed more than 300 times over the period 2009 – 2012 by 3 different accredited laboratories. The ambient background concentrations of dissolved trace elements (<0.45 µm) in surface water are summarised in Figure 9. For the elements Be, Cu, Hg, Mo, Se, Sn, Ti and Tl, more than 90 % of the reported values were lower than the limit of quantification (LoQ) of the laboratory, therefore a (median) LoQ is reported in Table 1. It should be noted that the LoQs used by accredited laboratories in environmental regulatory monitoring are related to the legal requirements and, as such, they do not necessarily reflect the instrumental power of detection attainable by ICP-MS (see further, results of round robin test performed in 2014). For the other elements and on average, less than 40 % of the reported values were lower than the LoQ of the laboratory. In order to calculate a mean concentration of each element for each of the locations, the approach as set by Directive 2009/90/CE (technical specifications for chemical analysis and monitoring of water status) was followed, *i.e.*, if the amount of an element in a given sample is below LoQ, the measurement result shall be set to half of the value of the LoQ for the calculation of the mean value.

3.5.1 Performance characteristics of ICP-MS method (EN 17294)

To further study real-life attainable LoQs by ICP-MS for the determination of the total element content in surface water and dissolved element content in groundwater in a regulatory monitoring context, a round robin test was recently (2014) organised amongst 14 accredited laboratories [40]. For this purpose, a synthetic sample was prepared containing typical concentrations of major elements and spiked with trace elements at a concentration level (where possible) below 30 % of the EQS values defined in the Flemish Environmental legislation. The surface water was asked to be acid digested according to EN ISO 15587-1:2002 (*aqua regia* digestion) and 10-fold diluted before measurement. The groundwater sample was analysed as such. For the determination of the LoQ, the laboratories were asked to digest and analyse the sample five-fold under reproducibility conditions. The LoQ was calculated as 6 times the standard deviation on the 5 independent determinations of the synthetic sample. The results of the round robin test are summarised in Table 2 and Table 3.

The derivation of the LoQ using this approach is to some extent related to the concentration level of the spike. For the determination of, *e.g.*, Zn in surface water, the median LoQ of 15 µg L^{-1} was derived based on the measurement of a spiked concentration of 10 µg L^{-1}. Taking into account that the EQS for Zn in surface water is 200 µg L^{-1}, this can be considered as fit-for-purpose. For some elements (Al, Fe and B) a significant bias was observed, which can be related to contamination. For the elements As, Se, Ni , V and Zn spiked at a concentration ≥ 1 µg L^{-1} , an RSD of > 40 % was observed. The synthetic groundwater sample was analysed without digestion and dilution, and this results in better inter-laboratory precision and attainable LOQs. These data illustrate that even to date, dealing with spectral and non-spectral interferences is still one of the main challenges in the routine adoption of ICP-MS as a monitoring method for surface water.

3.5.2 Harmonized implementation of European regulatory monitoring requirements

When evaluating toxicity data to derive quality standards for “heavy metals”, total element concentrations are usually not directly related to ecotoxicological effects because many abiotic and biotic processes can modify the availability of elements, even rendering them unavailable for uptake. This means that the fraction available for uptake and thus potentially toxic may be a very small part of the total amount of element present. The Water Framework Directive explicitly acknowledges the issues of (bio)availability and naturally occurring concentrations for elements [59]. Ideally, the derivation of EQS for “heavy metals” requires an explicit consideration of (bio)availability using speciation models or, failing that, to utilise dissolved concentrations instead of total concentrations. Dissolved elements are operationally defined as filtered through 0.45 µm membrane filter in surface water. Today’s distinction between the dissolved and particulate phases in (geo)chemistry can be traced back to the application of 0.5 µm cellulose acetate membrane filters to ocean waters in 1952 [60]. Since then, different studies called for relinquishing the misleading delineation of particulate and dissolved phases at about 0.45 µm, but this operational definition has become firmly established by now [61,62].

Until now, assessment of the sampling protocol, not commonly included in quality control schemes, has received little attention, and this may well become critical for implementation of legislation such as the EU Water Framework Directive. Where contaminant levels fluctuate, optimisation of the sampling frequency is of utmost importance, and 12 equally spaced-sampling events per year may not provide representative information (*e.g.*, flood events). One possible solution is the use of passive sampling devices to provide time-weighted average (TWA) pollutant concentrations in water [63]. Passive samplers such as the diffusive gradient in thin film (DGT) devices and Chemcatcher accumulate a labile fraction of metals by diffusion with minimal disturbance of the system and provide more representative and toxicologically more relevant metal concentrations. It is now being recognised that passive samplers can play a valuable role in monitoring water quality within a legislative framework such as the European Union’s Water Framework Directive [64,65]. The data from these devices can be used alongside the results obtained from conventional spot sampling to improve risk assessments and to provide information required to take decisions on undertaking potentially expensive remedial actions. It is expected that the aquatic monitoring sector will follow a transition similar to that which occurred in air monitoring, where data obtained from passive samplers or on-line measurement devices can be used in a complementary manner within a legal framework. But, as stated earlier, the introduction of harmonised and standardised analytical methods tends to delay the acceptance and use of new and innovative monitoring / screening methods.

3.6 Ambient background concentration of elements in groundwater

Aquifers from the same typology can have strongly different groundwater chemistry and natural background levels are rather a range of values than single values. M. Coetsiers *et al.* attempted to derive natural background levels for four aquifers in Flanders of the sand and gravel typology as the

90th and 97.7th percentile of a carefully chosen dataset to approach the natural groundwater composition [25]. The range of natural background levels (90th percentile) in these four aquifers (fluvial Pleistocene and Tertiary marine) are summarised in Table 4.

The range of background levels, regulatory defined for each of the 42 groundwater bodies defined in the Flanders region, are also represented in Table 4. The values of regulatory background levels, represent the 90th percentile of the measurements performed at background locations per groundwater body.

The median ambient background levels (also reported in Table 4) were derived for each groundwater body as the 90th percentile of the results of the groundwater monitoring campaign of 2006. Different accredited laboratories were involved in this regulatory monitoring campaign. Over the years, different analytical techniques (ICP-AES, ICP-MS and graphite furnace AAS) have been used for groundwater monitoring. In the 2006 monitoring campaign, most of the trace element concentrations determined in more than 2600 groundwater samples were reported by the accredited laboratory as lower than the LoQ of the laboratory (*inter alia* caused by the use of different analytical techniques, such as ICP-AES). Based on this dataset, the expected median background concentrations for dissolved trace elements in groundwater are < 0.05 µg L^{-1} for Hg, < 0.1 µg L^{-1} for Cd, < 1 µg L^{-1} for Pb, Cr and Cu, < 10 µg L^{-1} for As and Ni and < 20 µg L^{-1} for Zn. For the major elements, a wide range is observed for the background levels in the different groundwater bodies (e.g., for Na, the concentration ranges from 5 to 5000 mg L^{-1}).

Of the more than 5000 filter screens, analysed during the 2011 monitoring campaign, 12% contained at least one element above the groundwater EQS (see Table 4). Values exceeding the corresponding EQS were mostly observed for B and As and do rather reflect geological variation than anthropogenic influence. Currently attainable LoQs for the determination of dissolved elements in groundwater by ICP-MS are summarised in Table 3. The given ranges of ambient background concentrations in groundwater (see Table 4) point to ICP-MS as the method of choice, as the superior power of detection combined with the wide linear dynamic range (determination of trace, *e.g.*, Cd, and major elements, *e.g.*, Na, in the same run) favours the use of ICP-MS over that of ICP-AES and GF-AAS.

4 Conclusion

The introduction of ICP-MS in environmental regulatory monitoring of elements under the impulse of standards developed by the European Committee for Standardization is undoubtedly the most important advance of the last decade. Because of the availability of ICP-MS instruments nowadays, it can be argued that the main hindrance to the implementation of the European monitoring requirements is not the technical feasibility of analysis at these concentration levels, but rather potential contamination during sampling, sample storage, sample handling, digestion and analysis. Furthermore, the use of more challenging sampling and analytical proficiency testing, the enhanced use of CRMs (if available) and of in-house matrix-matched QC materials are required to further address the performance characteristics of the monitoring methods and to improve the comparability of data. Another key issue here, is the training and experience of staff taking samples, which traditionally an area that has – compared to analytical methods - less well developed/standardised. Two additional comments with respect to a harmonised implementation of the European monitoring requirements may be formulated at this point. First, as for most monitoring methods, results obtained are operationally-defined. The protocol, *e.g.,* acid digestion, 0.45 µm filtration*,* ... governs to some extent the answer, and while this may facilitate comparability of results acquired across Europe, data generated may have little relevance to bioavailable metal concentration. Second, more harmonisation in communication and reporting of the chemical environmental status between member states is needed to compare regulatory monitoring data on a European scale, *e.g.*, choice of sampling locations (*e.g.*, rural versus industrial) and type of sample (*e.g.*, biota versus water column).

The range of elemental background concentration estimates, derived from the different examples of Flemish regulatory monitoring, illustrates a good match with the power of detection of ICP-MS instruments. Additionally, for the determination of elements in soil and river sediment and with the incorporation of Hg in CEN/TS 16171 as one of the elements determinable by ICP-MS, the use of ICP-MS in future regulatory monitoring will certainly be favoured. One must keep in mind that the choice of the acid digestion procedure will have implications on the measured concentration of some elements (*e.g., aqua regia* versus additional use of HF).

In support of the European Water Framework Directive, ICP-MS (EN 17294) became the only method of choice for chemical analysis and monitoring of dissolved elements in surface water. More monitoring studies using ICP-MS and with focus on low level determination of elements are needed to refine the derived estimates of ambient background concentrations (now often reported as < LoQ). However, dealing with spectral and non-spectral interferences is still one of the main challenges in the routine adoption of ICP-MS as a monitoring method. For the determination of concentrations in surface and groundwater, it can be argued that the risk of sample contamination nowadays represents a far greater challenge than the instrumental LoDs attainable with ICP-MS.

The same holds true for the determination of elements in fine particulates and atmospheric deposition: sampling and contamination-free acid digestion are considered the most critical steps for accurate trace environmental monitoring. The European standard methods for the determination of elements in ambient air (EN 14902 and EN 15841) prescribes nitric acid digestion (in combination with H_2O_2 or traces HF), which also favours the use of ICP-MS as sensitive and multi-elemental determination method.

This being said, it is also clear that the panoramic analysis capabilities of ICP-MS are not yet fully exploited in current environmental monitoring studies with respect to its linear dynamic range and multi-element capabilities [57]. The determination of “heavy metals” in environmental monitoring has traditionally focused on a relative small number of elements (e.g., As, Cd, Hg, Pb), but it is to be expected that future regulatory monitoring will include more elements (holistic approach) and that the panoramic analysis capabilities of ICP-MS will be further exploited. In addition, the labour-intensive steps of preparation of calibration standards, dilution of samples and the addition of internal standards can be automated by using an in-line auto-dilution/auto-calibration sample delivery system, which could make this approach well-suited for the demands of a high-throughput environmental laboratory. Furthermore, it significantly lowers the risk of contamination of the sample, standards or blanks, because all these functions are being carried out in-line, with no manual intervention by the analyst. Also recent innovative sample introduction systems, e.g., an automated micro injection system or a high matrix introduction (HMI) system, are expected to further broaden the scope of ICP-MS applications for the analysis of high dissolved solids samples (*e.g.*, soil digests) as well.

Last but not least, the range of derived estimates of background concentrations of elements can be used to assess future anthropogenic influences within an EU regulatory monitoring context. However, as elements do not disappear, but are rather dispersed from one environmental compartment into another, the chemical nature and quantity of the relevant element species in a matrix, its physical and chemical association, rather than the (pseudo) total element concentration is governing the toxicological impact of that element. Therefore, supplementary knowledge on speciation is needed for sufficient information for environmental risk assessment.

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Figure 1: Locations of sampling sites for determination of ambient background values in the Flemish region of Belgium.

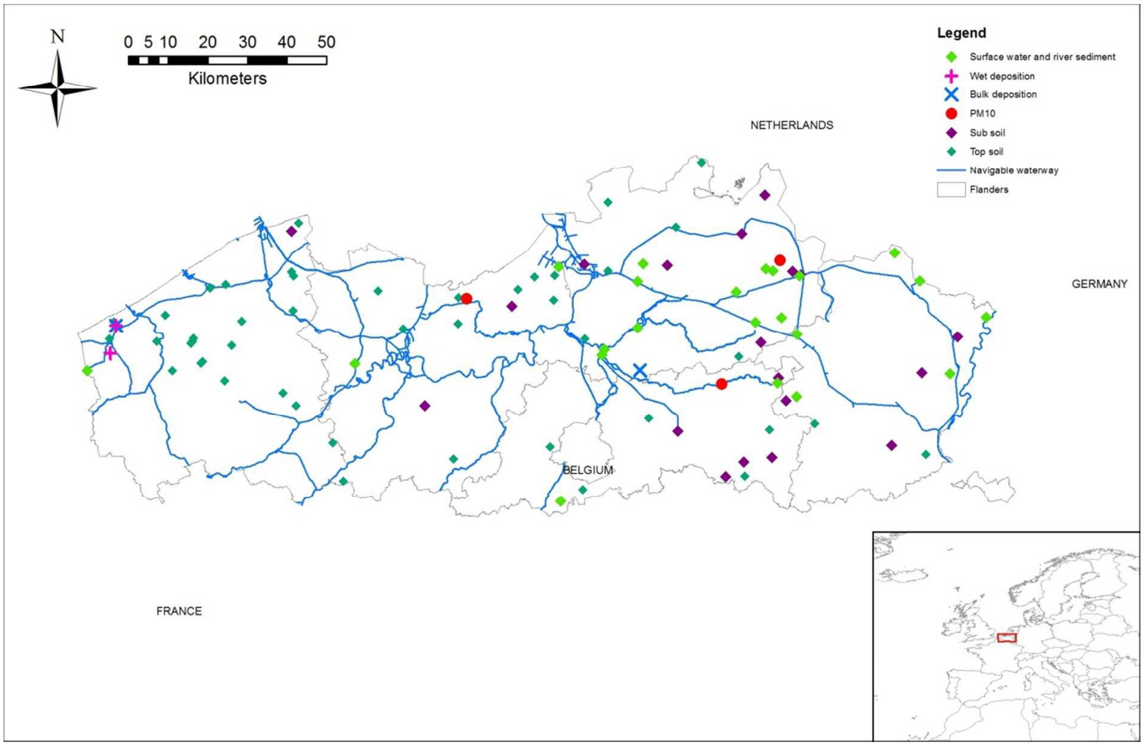
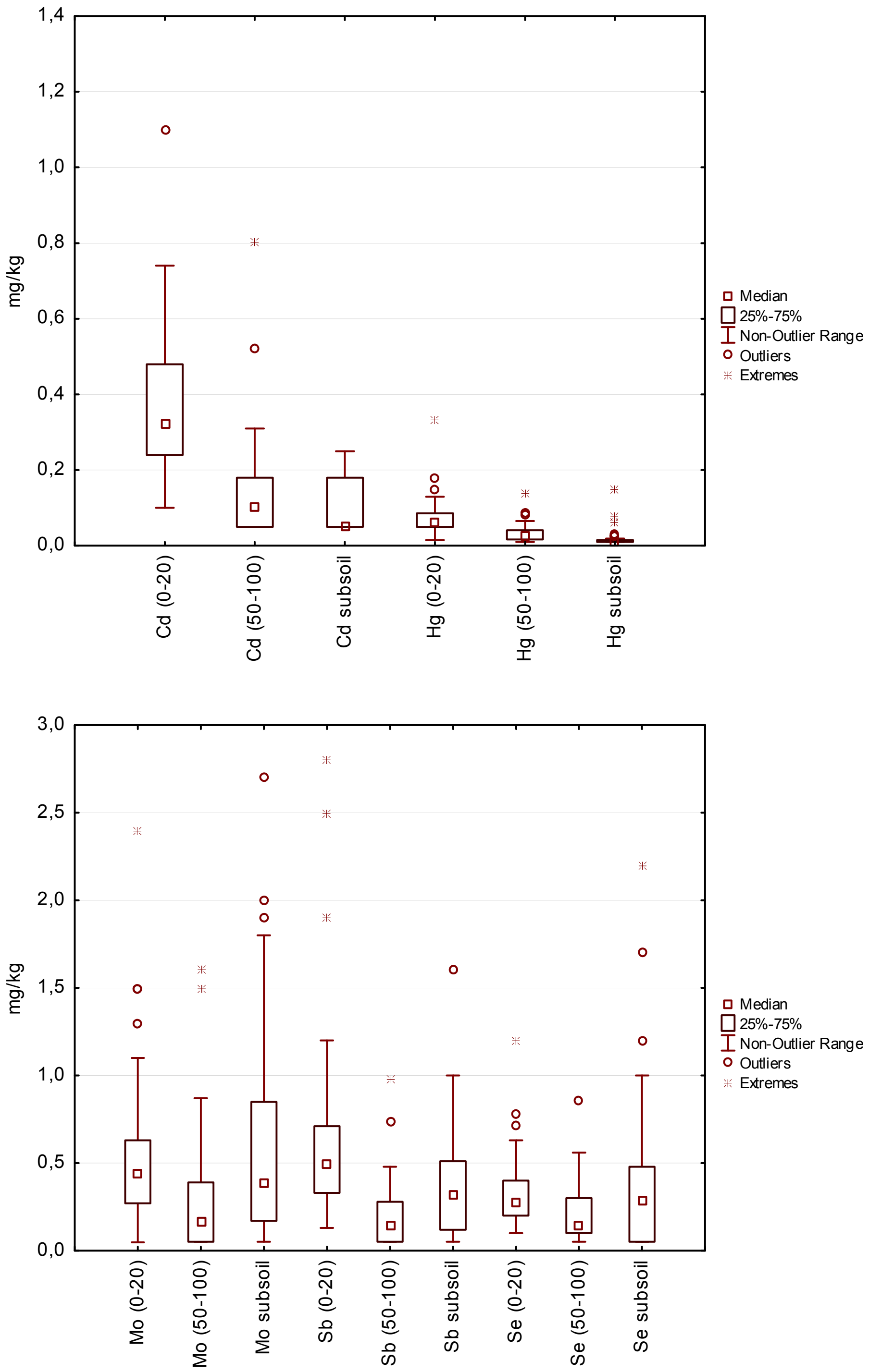
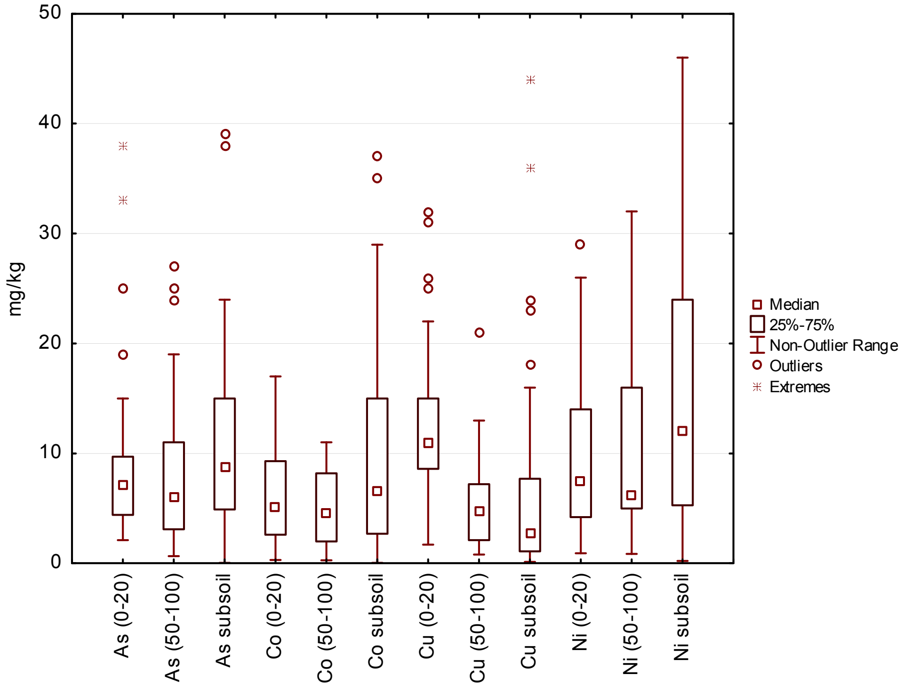


Figure 2 (A,B,C,D): Elemental ambient background concentrations (mg kg^{-1}) in Flemish soils following HNO_3/HCl digestion and analysis by sector-field ICP-MS (45 topsoil samples (0-20 cm and 50-100 cm) and 45 subsoil samples (Tertiary deposits), collected at different locations (data courtesy of OVAM [33]).




mg/kg
0
10
20
30
40
50
As (0-20)
As (50-100)
As subsoil
Co (0-20)
Co (50-100)
Co subsoil
Cu (0-20)
Cu (50-100)
Cu subsoil
Ni (0-20)
Ni (50-100)
Ni subsoil
Median
25%-75%
Non-Outlier Range
Outliers
Extremes

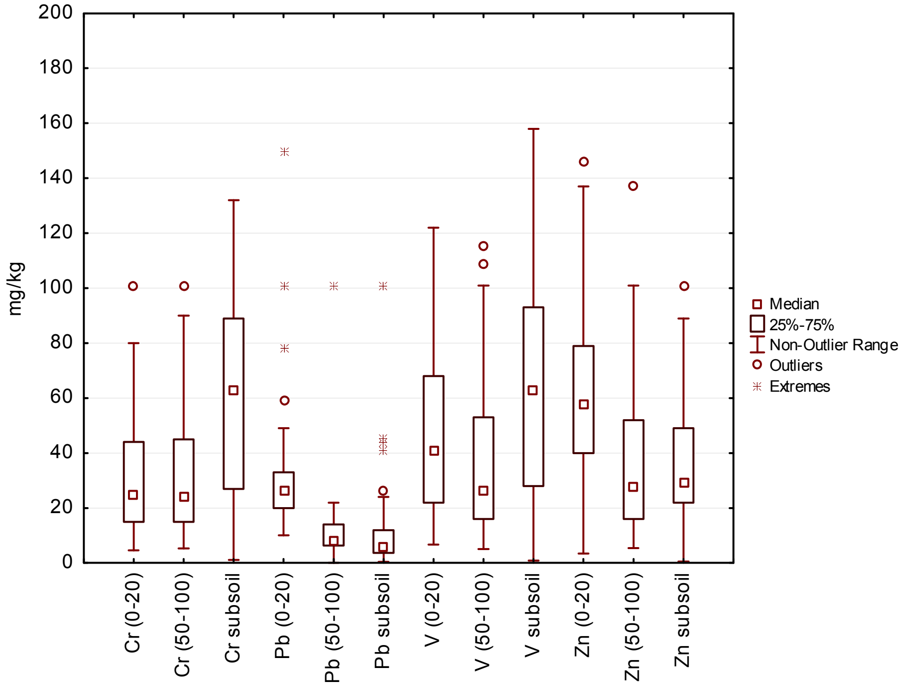

mg/kg
0
20
40
60
80
100
120
140
160
180
200
Cr (0-20)
Cr (50-100)
Cr subsoil
Pb (0-20)
Pb (50-100)
Pb subsoil
V (0-20)
V (50-100)
V subsoil
Zn (0-20)
Zn (50-100)
Zn subsoil
Median
25%-75%
Non-Outlier Range
Outliers
Extremes

Figure 3: Comparison between determination of Cr in 90 topsoil samples and 45 subsoil samples after *aqua regia* and HNO_3/HCl/HF digestion, respectively (data courtesy of OVAM).

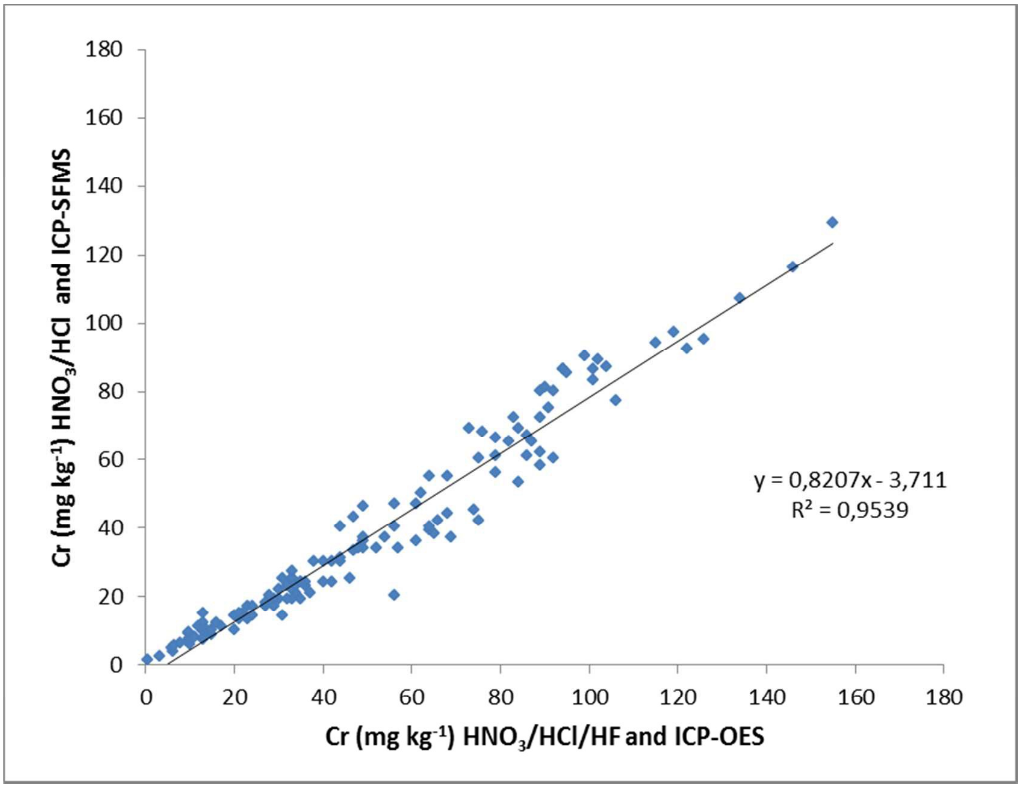
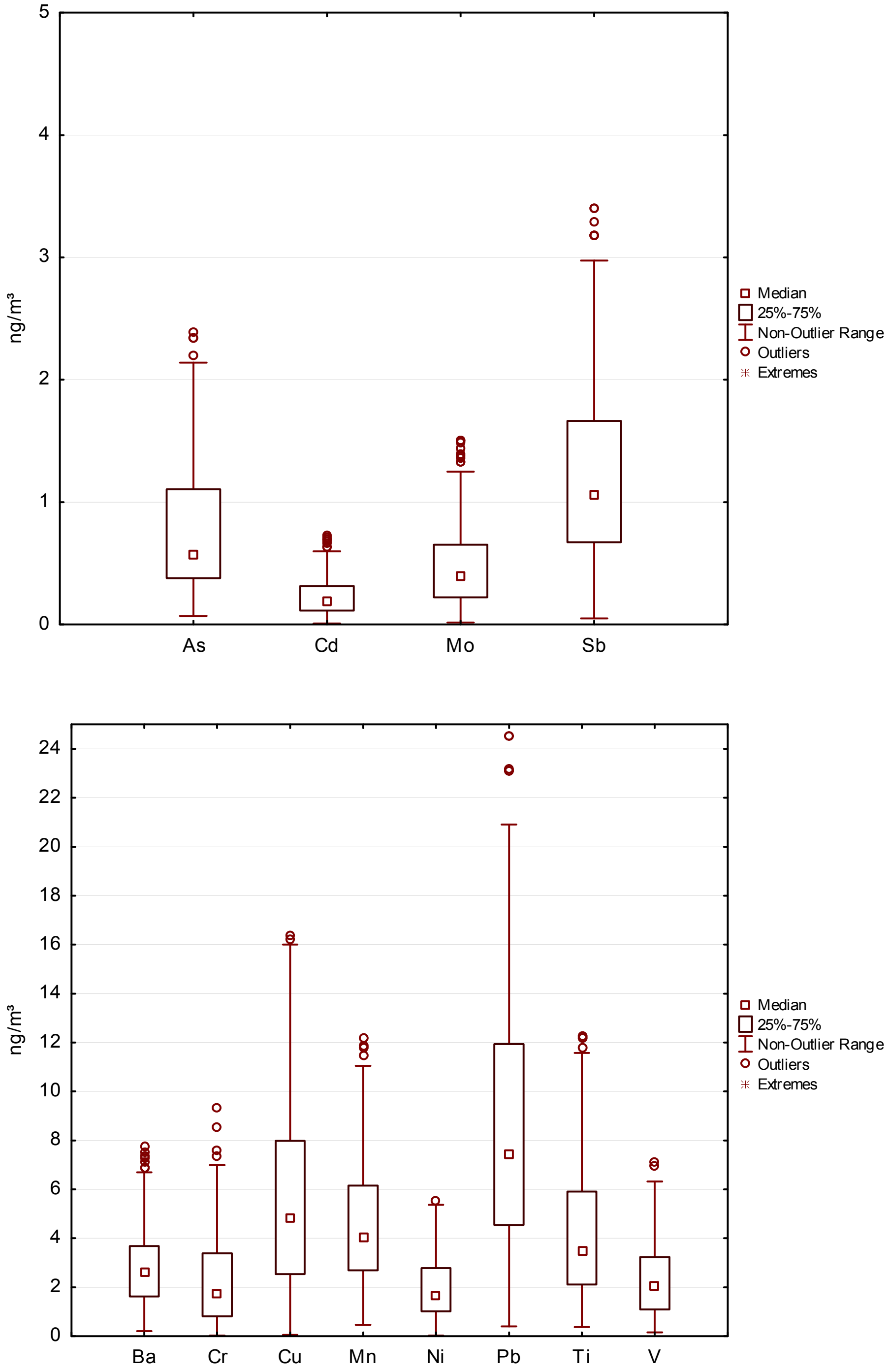


Figure 4 (A,B,C): Ambient background concentrations (ng m^{-3}) of elements in PM$_{10}$ in Flanders, determined with ICP-MS after acid digestion according to EN 14902 (250 PM$_{10}$ samples collected at 3 different locations, data courtesy of VMM [46-48]).



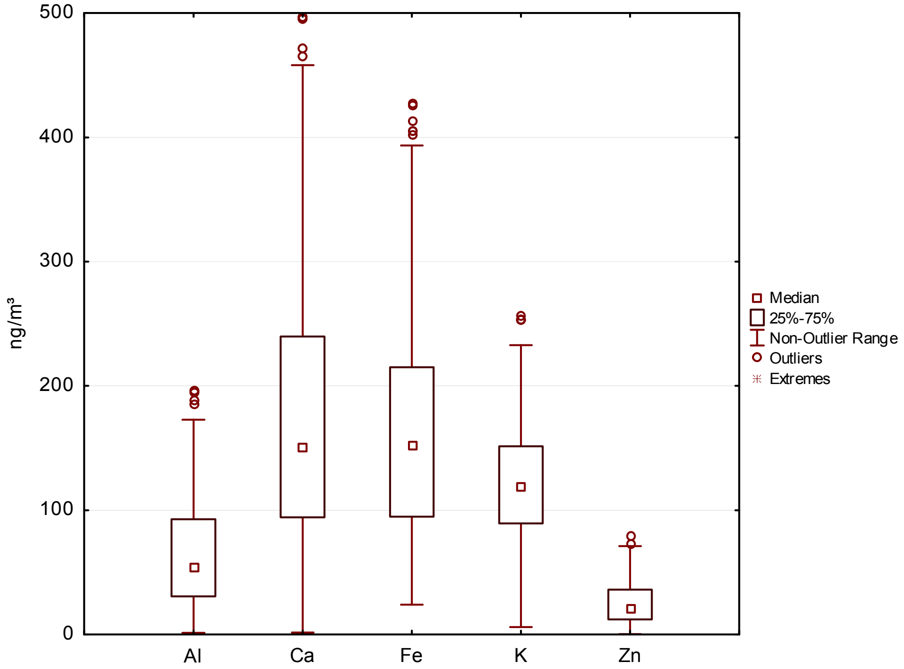

500
400
300
200
100
0
ng/m³
Al
Ca
Fe
K
Zn
Median
25%-75%
Non-Outlier Range
Outliers
Extremes

Figure 5 (A,B): Ambient background concentrations (µg $m^{-2}.day^{-1}$) of elements in total atmospheric deposition in Flanders, determined with ICP-MS after acid digestion (52 samples collected at Koksijde and Bonheiden, data courtesy of VMM).

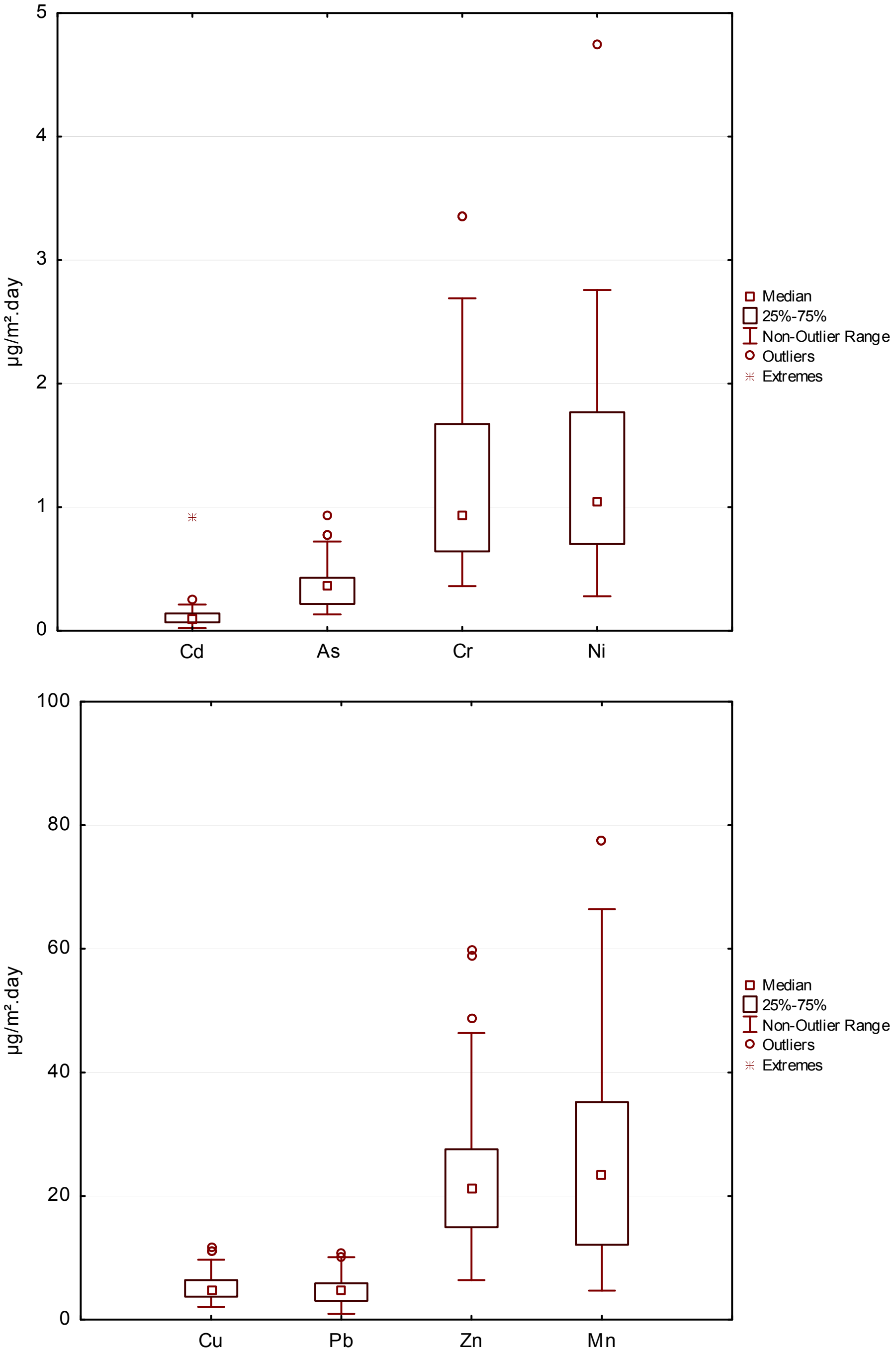


Figure 6 (A,B): Ambient background concentrations (µg m^{-2}.day^{-1}) of elements in wet atmospheric deposition in Flanders, determined with ICP-MS after acid digestion (75 samples collected at Koksijde, data courtesy of VMM).

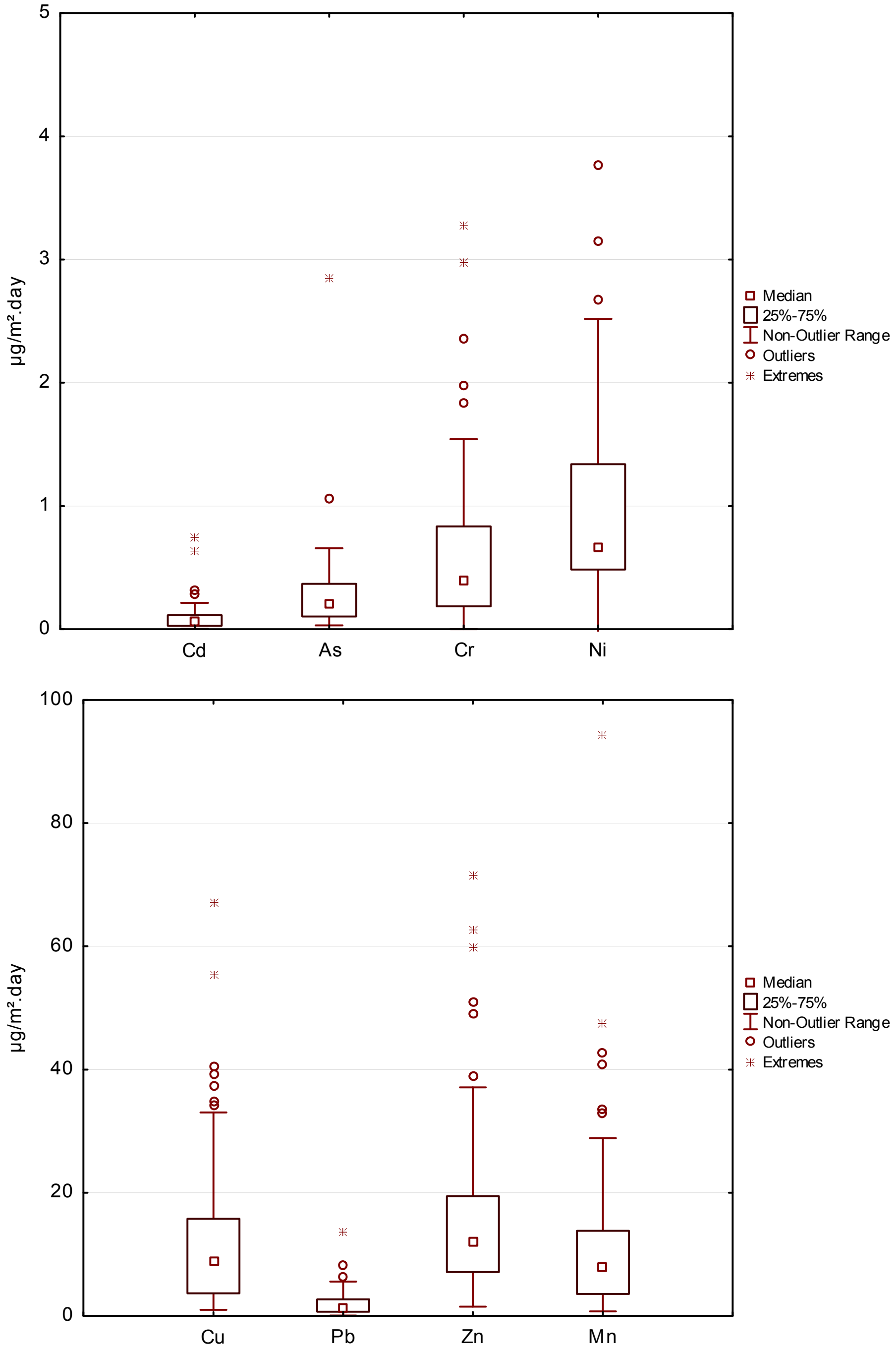
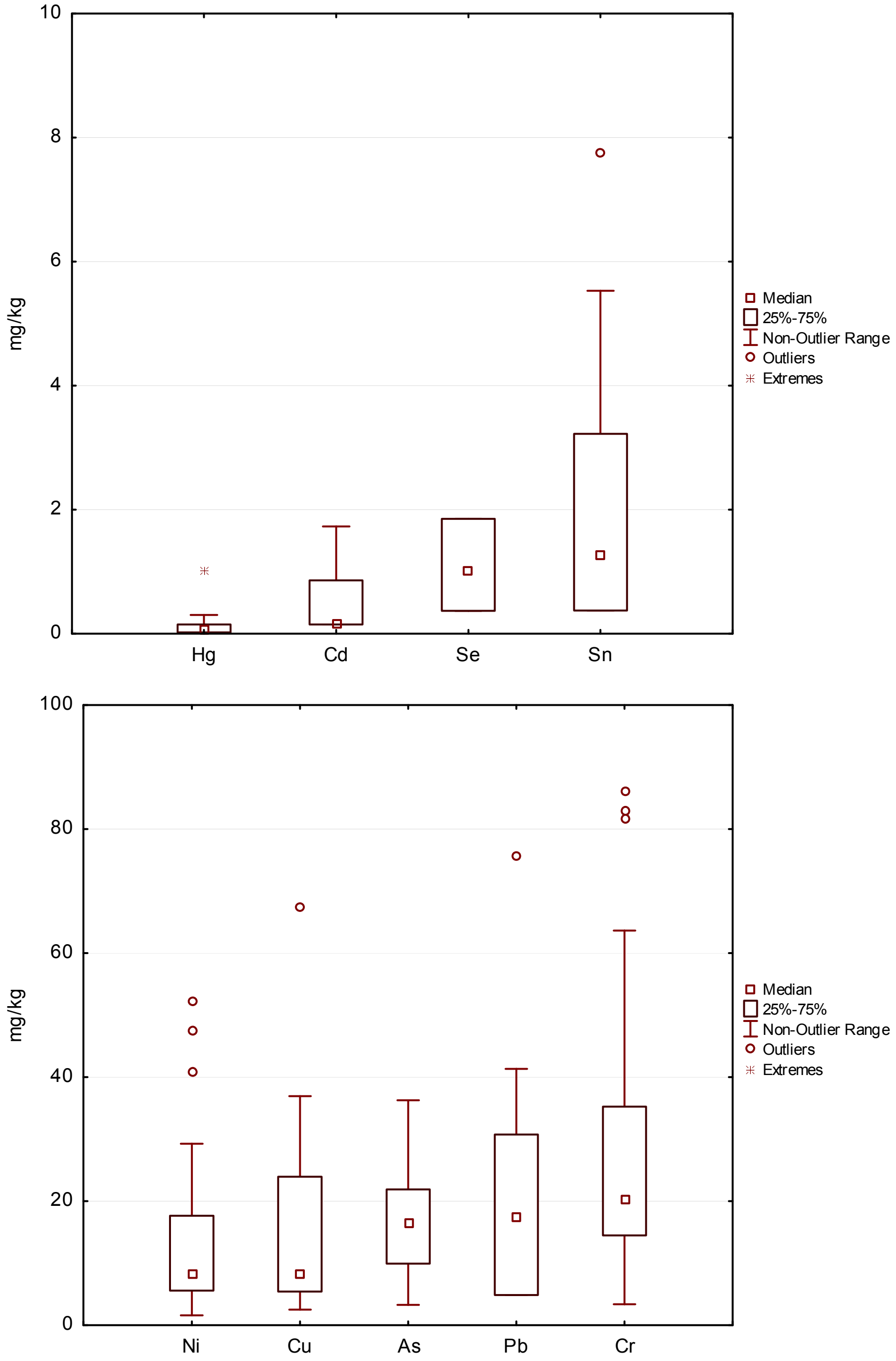


Figure 7 (A,B,C): Ambient background concentrations (mg kg^{-1}) of elements in river sediment in Flanders, determined with ICP-MS after *aqua regia* digestion according to CEN/TS 16171 (samples collected at 22 different locations, see Figure 1: Locations of sampling sites for determination of ambient background values in the Flemish region of Belgium)(data courtesy of VMM).



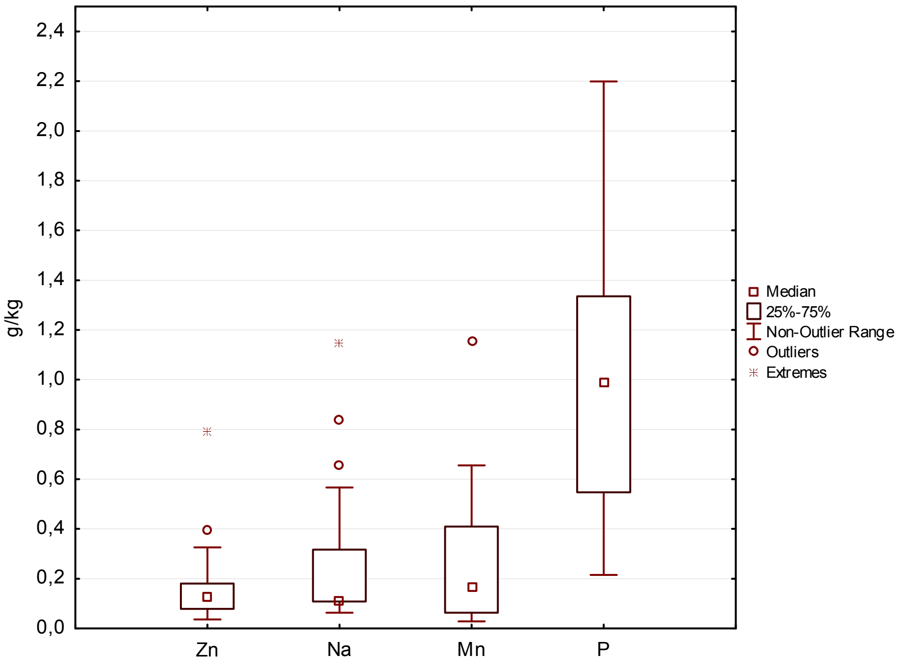

2,4
2,2
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
g/kg
Zn
Na
Mn
P
Median
25%-75%
Non-Outlier Range
Outliers
Extremes

Figure 8: Ambient background concentration (mg kg^{-1}) of matrix elements in river sediment in Flanders, determined with ICP-MS after *aqua regia* digestion according to CEN/TS 16171 (samples collected at 22 different locations)(data courtesy of VMM).

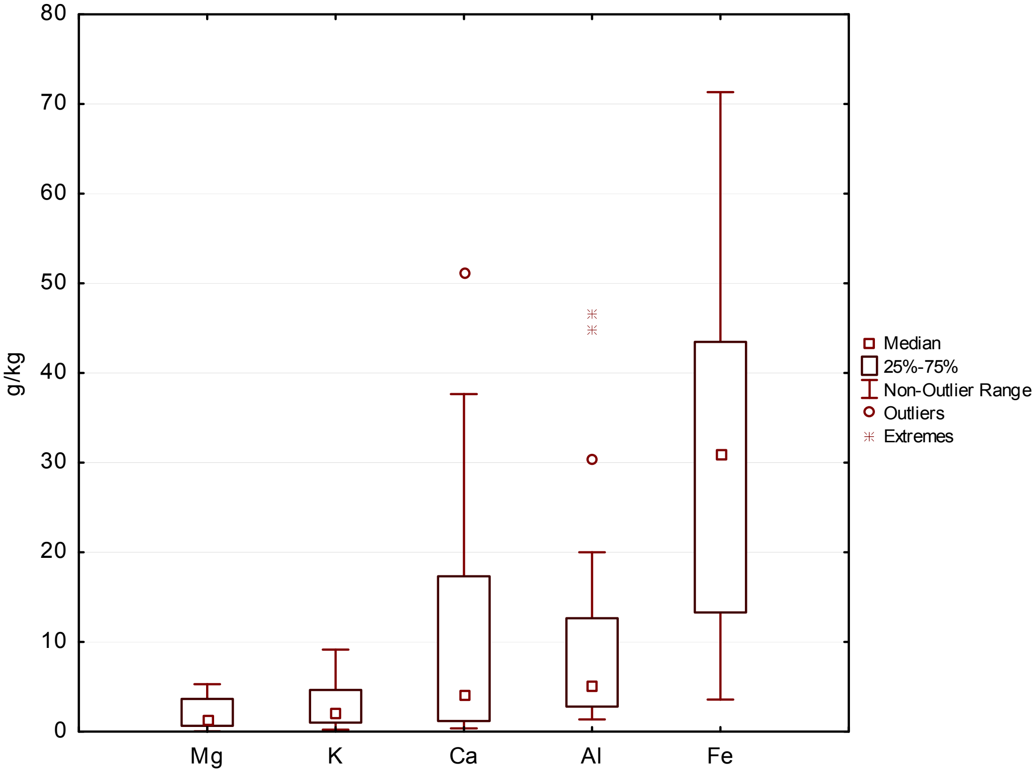
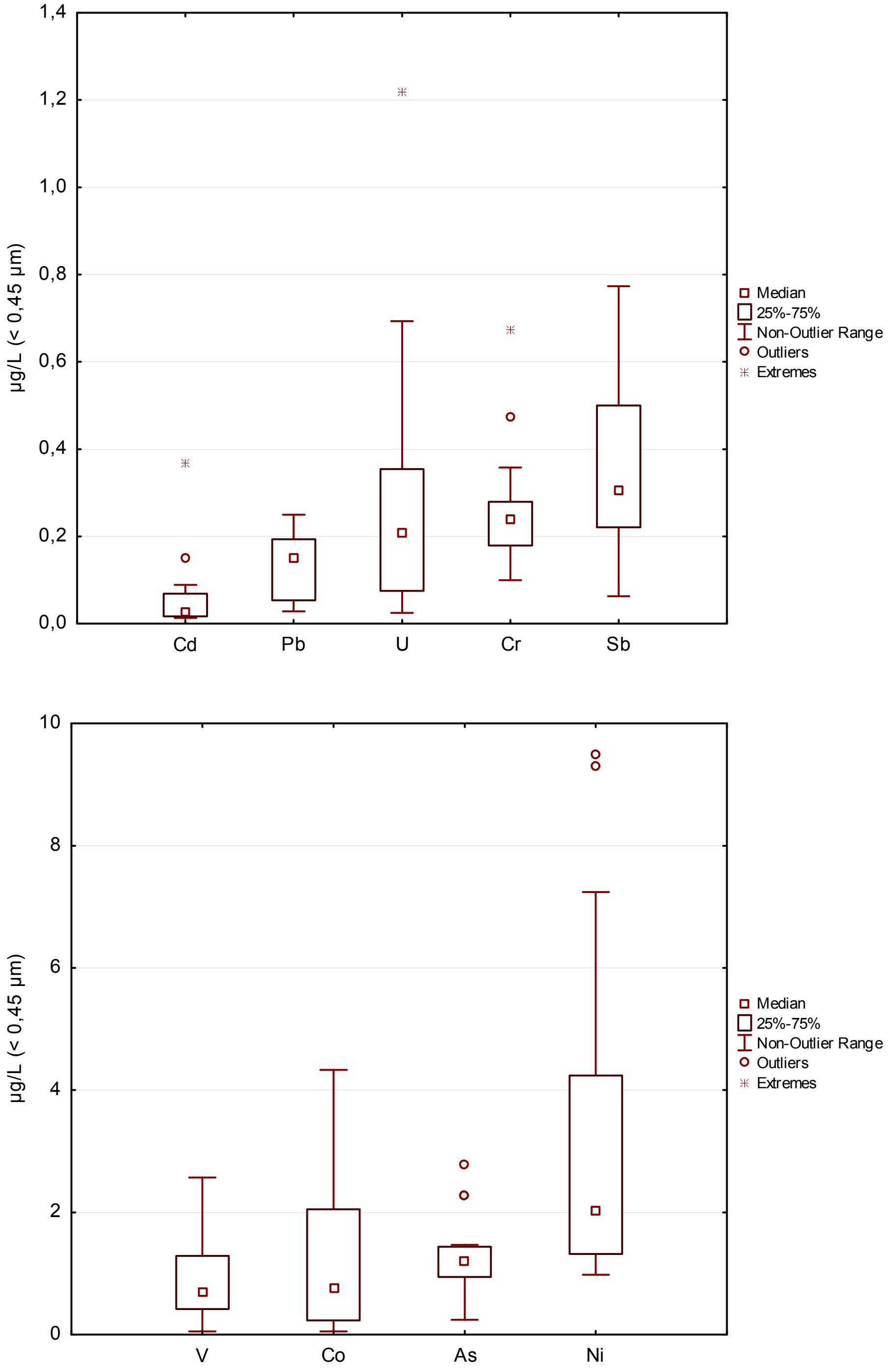
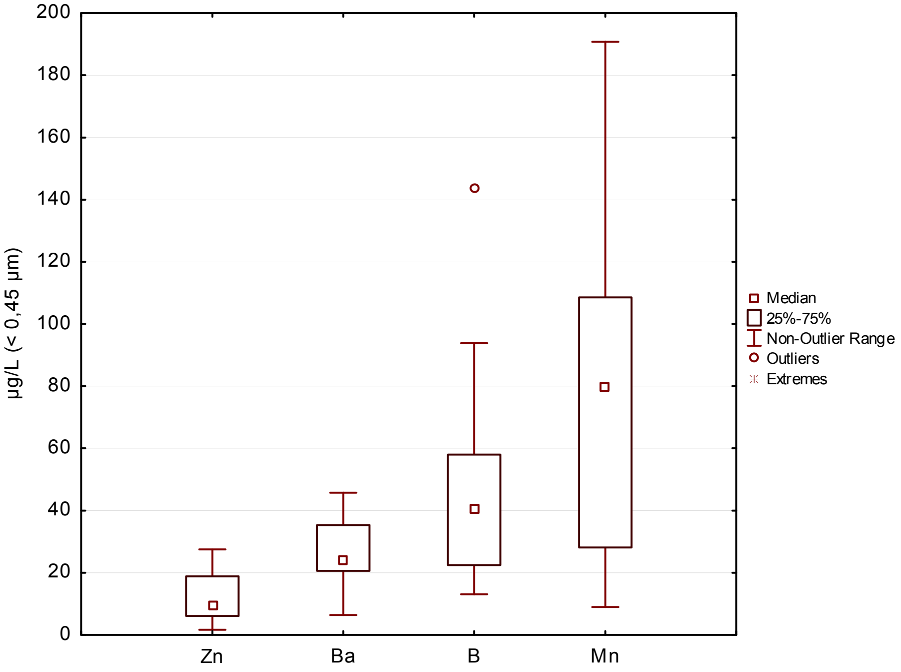


Figure 9 (A,B,C): Ambient background concentrations (µg L^{-1}) of dissolved trace elements (<0,45 µm) in Flemish surface water as determined with ICP-MS (average of 300 samples collected at 22 different locations) (data courtesy of VMM).





808

809

810

811

Table 1: Estimates of median ambient background concentrations of elements present in the different environmental compartments in Flanders using (ICP-MS based) EN standard procedures.

	lithosphere			atmosphere			hydrosphere		
	EN 16174 CEN/TS 16171	EN 16174 CEN/TS 16171	EN 16174 CEN/TS 16171	EN 14902	EN 15841	EN 15841	EN 16174 CEN/TS 16171	EN17294	EN17294
	0-20 cm	50-100 cm	tertiary	PM$_{10}$	bulk deposition	wet deposition	river sediment	surface water	ground-water
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	ng m^{-3}	µg m^2.day^{-1}	µg m^2.day^{-1}	mg kg^{-1}	µg L^{-1} *(< 0.45 µm)*	µg L^{-1} (<0.45 µm)
As	7.2	6.1	8.8	0.61	0.37	0.21	17	1.2	< 10
Ba				2.7				24	
Cd	0.32	0.10	0.050	0.20	0.098	0.059	0.15	0.027	< 0.1
Co	5.2	4.6	6.6					0.75	
Cr	25	24	62	2.0	0.94	0.40	20	0.24	< 1
Cu	11	4.7	2.7	5.0	4.6	9.0	8.2	<2	< 1
Hg	0.062[a]	0.027[a]	0.01[a]	0.7[b]		0.025[c]	0.052[d]	< 0.01[e]	< 0.05
Mn				4.3	23	8.1	169	80	
Mo	0.44	0.16	0.39	0.44				< 2.5	
Ni	7.4	6.3	12	1.8	1.0	0.67	8.2	2.0	< 10
Pb	26	8.3	6.1	8.1	4.6	1.4	17	0.15	
Sb	0.5	0.14	0.32	1.1				0.31	
Se	0.28	0.14	0.29				1.0	< 2	
Sn							1.3	< 0.5	
Ti				3.6				< 1	
V	40	26	62	2.2				0.71	
Zn	57	26	29	22	21	12	125	9.6	< 20

[a] CEN/TS 16175-2:2013, [b] EN 15852:2010, [c] EN 15853:2010, [d] EPA 7473:1998, [e] EN 12846:2012

Table 2: results of round robin test for the determination of total element contents in a synthetic matrix-matched surface water by ICP-MS. Each regulatory EQS represents the environmental quality standard for the total content of that element in Flemish surface water; The median concentration represents the 50 percentile value of the reported concentration by the laboratories; σ_{group} represents the calculated standard deviation; $RSD_{\%}$ represents the calculated relative standard deviation; n is the number of results; median LoQ represents the 50 percentile value of the reported LoQs by the laboratories (LoQ was calculated as 6*st. dev. on five independent measurements of the surface water).

Element	Regulatory EQS	spiked concentration	median concentration	σ_{group}	$RSD_{\%}$	n	median LoQ
	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	%		µg L^{-1}
Aluminium		10	19.7	13.3	68	11	23.1
Antimony	100	10	10.1	1.0	10	14	2.4
Arsenic	5	1	1.3	0.67	51	13	0.91
Barium	70	10	10.5	0.73	7	13	1.9
Beryllium	0.1	0.1	0.09	0.06	66	8	0.11
Boron	700	10	26.1	20.5	78	10	53.1
Cadmium	0.8	0.1	0.13	0.05	36	13	0.2
Cerium		1	1.2	0.18	16	8	0.2
Chromium	50	10	10.5	1.3	13	13	3.7
Iron		10	19.7	9.3	48	11	32.9
Cobalt	0.6	0.1	0.12	0.04	30	11	0.19
Cupper	50	10	12.3	2.6	21	13	11.5
Lead	50	10	10.2	0.86	8	14	1.6
Manganese		10	11.1	1.6	15	14	3.1
Molybdenum	350	10	10.5	1.3	13	12	1.9
Nickel	30	1	1.2	0.59	48	14	3.3
Selenium	3	1	0.93	0.40	43	12	1.3
Tellurium	100	1	0.90	0.26	29	9	0.86
Thallium	0.2	0.1	0.13	0.06	44	7	0.10
Tin	40	10	9.8	1.3	13	10	2.6
Titanium	100	10	11.0	2.5	23	9	10.5
Uranium	1	0.1	0.11	0.03	23	9	0.05
Vanadium	5	1	1.1	0.62	55	9	0.94
Silver	0.4	0.1	0.14	0.06	40	10	0.15
Zinc	200	10	14.6	7.8	54	12	14.5
matrix elements		mg L^{-1}					
Ca		**100**					
Cl		50					
P		0.5					
S		25					
Mg		10					

Na	25
K	5
C	10

Table 3: results of round robin test for the determination of dissolved element contents in a synthetic matrix-matched groundwater by ICP-MS. Each regulatory EQS represents the environmental quality standard for the dissolved content for that element in Flemish groundwater; the median concentration represents the 50 percentile value of the reported concentration by the laboratories; σ_{group} represents the calculated standard deviation; $RSD_{\%}$ represents the calculated relative standard deviation; n is the number of results; median LoQ represents the 50 percentile value of the reported LoQs by the laboratories (LoQ was calculated as 6*st. dev. on five independent measurements of the groundwater).

Element	Regulatory EQS	spiked concentration	median concentration	σ_{group}	$RSD_{\%}$	n	median LoQ
	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	%		µg L^{-1}
Aluminium		25	26.0	2.5	10	12	5.6
Antimony	10	2.5	2.55	0.26	10	15	0.56
Arsenic	20	2.5	2.69	0.20	8	15	0.57
Barium	1000	25	25.5	1.5	6	14	3.4
Boron	1000	25	24.2	5.0	21	12	8.3
Cadmium	5	0.25	0.25	0.02	9	15	0.05
Chromium	50	2.5	2.52	0.17	7	14	0.40
Cobalt		2.5	2.55	0.13	5	14	0.40
Cupper	100	2.5	2.39	0.27	11	15	0.65
Lead	20	2.5	2.49	0.19	8	15	0.26
Manganese	1000	25	26.1	1.0	4	15	2.7
nickel	40	2.5	2.47	0.20	8	15	0.74
Selenium	10	2.5	2.51	0.25	10	15	0.95
Zinc	500	25	25.4	1.4	5	14	4.4
matrix elements		mg L^{-1}					
Ca		100					
Cl		50					
P		0.05					
S		25					
Mg		10					
Na		25					
K		5					
C		5					

Table 4: Range of 90th percentile concentrations in Fluvial Pleistocene and Tertiary marine aquifers, median ambient background concentrations derived from regulatory monitoring (2006), range of regulatory background levels and environmental quality standards (EQS) for dissolved elements in Flemish groundwater.

	Fluvial Pleistocene / Tertiary marine aquifers	**Groundwater monitoring 2006**	**Regulatory Background levels**	**Regulatory EQS**
	Range of 90th percentile	Median	Range of 90th percentile	
	(< 0.45 µm)	*(< 0.45 µm)*	*(< 0.45 µm)*	
	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
As	5.6 - 30	< 10	1 - 60	20
B	0.3 - 1.2			1000
Cd	0.12 - 0.5	< 0.1	0.05 - 1	5
Cr	0.8 - 4	< 1	1 - 37	50
Cu	5 - 10.2	<1	0.5 - 7	100
Hg	0.05 - 0.25	< 0.05	0.03 - 0.5	1
Ni	3.7 - 39	< 10	5 - 60	40
Pb	0.5 - 5	< 1	1 - 18	20
Sb	0.03 - 1			
Zn	26 - 260	< 20	16 - 250	500
	mg L^{-1}	mg L^{-1}	mg L^{-1}	
Al	0.01 - 1.5	< 0.1	0.01 - 0.8	
Ca	73 - 200	79	4 - 700	
Fe	5 - 44	2.3	0.12 - 50	
K	10 - 36	3.5	3 - 200	
Mg	12 - 39	10	2 - 800	
Na	38 - 320	22	12 - 6000	
Mn	0.3 - 1.3	0.26	0.02 - 2.2	