



Groundwater quality changes in peri-urban areas of the Walloon region of Belgium

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ABSTRACT

An extensive survey of groundwater quality was performed at the regional scale in peri-urban and industrial contexts of the Walloon Region (Belgium). To this end, 243 sampling locations from 8 areas located in different geological contexts and different peri-urban areas of the region were sampled outside pollution hotspots related to contaminated sites. Each groundwater sample was analyzed for 19 inorganic trace elements, 59 organic micro-pollutants and 8 major and minor elements. Five physico-chemical parameters were measured in the field, at the time of sampling to determine the environmental conditions prevailing in groundwater. Existing groundwater chemical data available outside such peri-urban and industrial areas were also compiled from existing groundwater quality databases for comparison. Most of the organic and inorganic pollutants are detected and their levels of occurrence are described statistically. Cumulative distribution function plots allow comparing the distributions of inorganic trace elements in and outside the urbanized and industrialized areas and among the different prevailing geological contexts. Two indicators are introduced, one quantifying the impact on inorganic trace elements of diffuse pollution in urban and industrial areas, the other reflecting the influence of lithology on concentrations in groundwater. Results show that the composition of groundwater is altered in peri-urban and industrial areas with increased concentrations for several organic pollutants and for most inorganic trace elements. However, the results clearly indicate that for the inorganic trace elements, anthropogenic influence is not limited to increased discharge of pollutants in the urban and industrial areas but also to significant changes in environmental conditions, with more reducing and acidic conditions observed in groundwater. The influence of lithology is also marked in the data set. From a more pragmatic point of view, the data set has been also used to derive upper limits of pollutant background concentrations to be used in decision-making related to the management of contaminated groundwater in urban and industrial environments in the Walloon Region.

1. Introduction

High population growth and industrial development has increased the demand for freshwater resources during last years and they are expected to become increasingly scarce in the future, partly due to climate change (Aslam et al., 2018). Urban aquifers are more and more considered as a valuable resource for water supply but also for industrial purposes in many countries such as Belgium (SPW-DGO3, 2016), Switzerland (Minnig et al., 2017), Germany (Hellauer et al., 2018) or Italy (Colombo et al., 2020; Pollicino et al., 2021), among others. Thus, conservation and protection of groundwater are key issues in the management of water resources.

Groundwater pollution is a serious issue because in many aquifers, groundwater quality is deteriorated, and thus, identifying the factors of its deterioration is of paramount importance. In particular, it is important to determine if the chemical substances of concern are really associated to exogenous anthropogenic pollution sources or if they have any geogenic origin and to determine the hydrogeochemical conditions that contribute to their occurrence in groundwater. On the one hand, many aquifers are impacted by several anthropogenic activities (Schirmer et al., 2013). In urban and industrial areas, pollution sources are of various types such as: atmospheric deposition, urban runoff, industrial or domestic wastewater discharges, industrial solid or liquid wastes, gas stations, landfill leakage, septic systems and road de-icing

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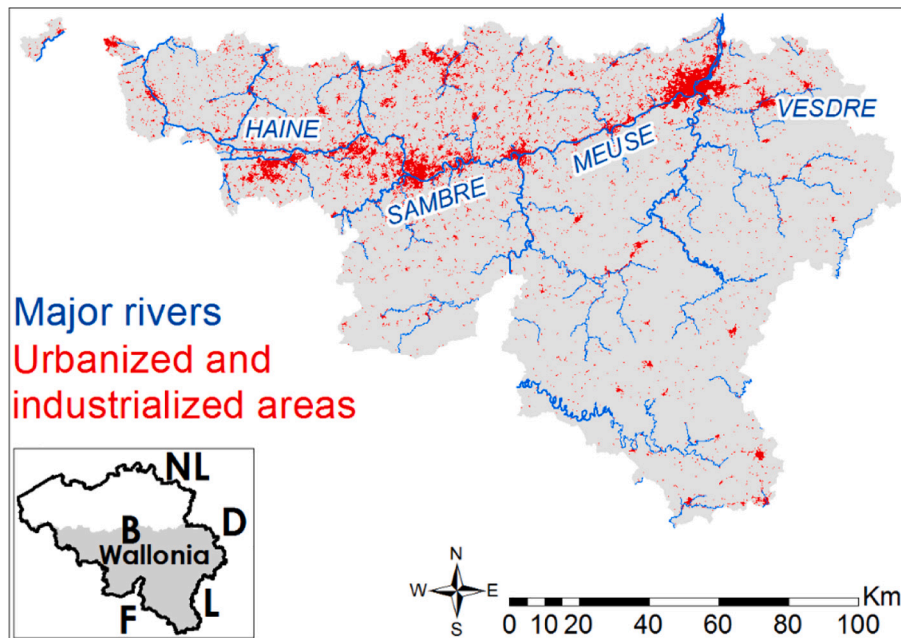


Fig. 1. : Major rivers and urban and industrial areas of Wallonia (southern Belgium) (B: Belgium, F: France, L: Luxembourg, NL: Netherlands, D: Germany) (Modified from SPW - DGO3 - DGARNE, 2015b).

salts, among others (Zhang et al., 2004; Vázquez-Suñé et al., 2010). The addition of point sources close to each other, diffuse pollution and multiple source pollution can also induce widespread contamination of groundwater resources (Rivett et al., 1990; Jamin et al., 2012; Sorichetta et al., 2012; Colombo et al., 2020; Pollicino et al., 2021). As a result, a wide array of organic (chlorinated volatile organic compounds (VOCs), non-chlorinated chlorinated VOCs and contaminants of emerging concern, among others), and inorganic pollutants (e.g., heavy metals) may enter aquifers leading to the deterioration of groundwater quality (Navarro and Carbonell, 2007; Rivett et al., 2012; Shepherd et al., 2006; Taylor et al., 2006; Serra-Roig et al., 2016; Pollicino et al., 2021).

On the other hand, groundwater quality can also be deteriorated by geogenic inorganic contaminants. In this case, their occurrence in groundwater may be due to geochemical changes in aquifer materials (e.g., high concentrations of the contaminants in the rock matrix dissolving during water-rock interactions) or related to changes towards more reducing conditions in the aquifer that facilitate the mobilization of contaminants in groundwater (Ghosh, 2017). Uranium, arsenic (As), radon and fluoride were found to be the most hazardous geogenic contaminants in terms of human health impacts (Grützmacher et al., 2013). Geogenic As contamination is a menace in the alluvial aquifers of the Ganges delta (India) and it is believed to be released from As-rich iron oxyhydroxides when dissolved oxygen is depleted from groundwater (Meharg et al., 2006).

As a result of both anthropogenic and geogenic factors, the value of the groundwater resource can be completely or partially lost when this freshwater resource is contaminated (Shanahan, 2009) and thereby limits its utility (Howard, 2002). Hence, to define the potential uses of groundwater, it is of paramount importance to assess its quality. For example, higher quality standards are expected if it is intended for drinking water purposes but groundwater also plays other key roles like delivering base flow to surface watercourses or in relation with aquatic and terrestrial groundwater-dependent ecosystems (EC, 2011, 2015).

The limit for a given chemical substance is set up by a number of organizations that have formulated guidelines of which the World Health Organization drinking water guidelines (WHO, 2017) or the European Groundwater Directive 2006/118/EC (EC, 2006) which also considers other quality objectives. Thus, the identification of the contaminants in the aquifers is the first step to assess its quality. This step is

particularly important in regions where groundwater is the main source of water supply such as the Walloon Region (southern part of Belgium) where groundwater abstraction represents 381.3 million m³ (2014 data) and 78.1% is devoted to drinking water purposes (SPW-DGO3, 2016). In rural areas of the Walloon Region, the impacts of diffuse groundwater pollution from agriculture have already been already studied concerning nitrate (Orban et al., 2010), pesticides (Hakoun et al., 2017) and greenhouse gases (Jurado et al., 2018; Nikolenko et al., 2019). However, there is a lack of data on the state of groundwater pollution in urban and industrial areas sites, and particularly in the sub-urban areas that are located around the most urbanized areas. Because of that, the suitability of groundwater for different uses in such transition zones between urban and rural areas remains uncertain.

In this context, the general objective of the present research is to assess the groundwater contamination level in urban and industrial contexts for the Walloon region of Belgium at the regional scale. More specifically, the objectives are to identify the most detected contaminants in groundwater, to describe statistically their levels of occurrence, and to discuss about mechanisms that can explain their occurrence in groundwater. The chemical compounds considered are inorganic trace elements and organic pollutants. From a more pragmatic point of view, this data set has been also used to derive an upper limit of background concentration levels to be used in decision-making related to the management of contaminated groundwater in urban and industrial environments. To this end, an extensive survey of groundwater contaminants was undertaken outside pollution hotspots specifically associated with polluted sites. Presented results are based on 243 samples collected in both shallow and deep aquifers from 8 areas located in different geological contexts and different urban and industrial contexts in Belgium and are compared to data collected outside urban and industrial contexts.

2. Description of the walloon region urban and industrial contexts

Major cities and industrial areas of Wallonia (southern Belgium) are located along a West-East alignment formed by the Haine, Sambre, Meuse and Vesdre rivers (Fig. 1). The main industrial cities are Charleroi and Liège, whose urban agglomeration had 291,000 and 501,000

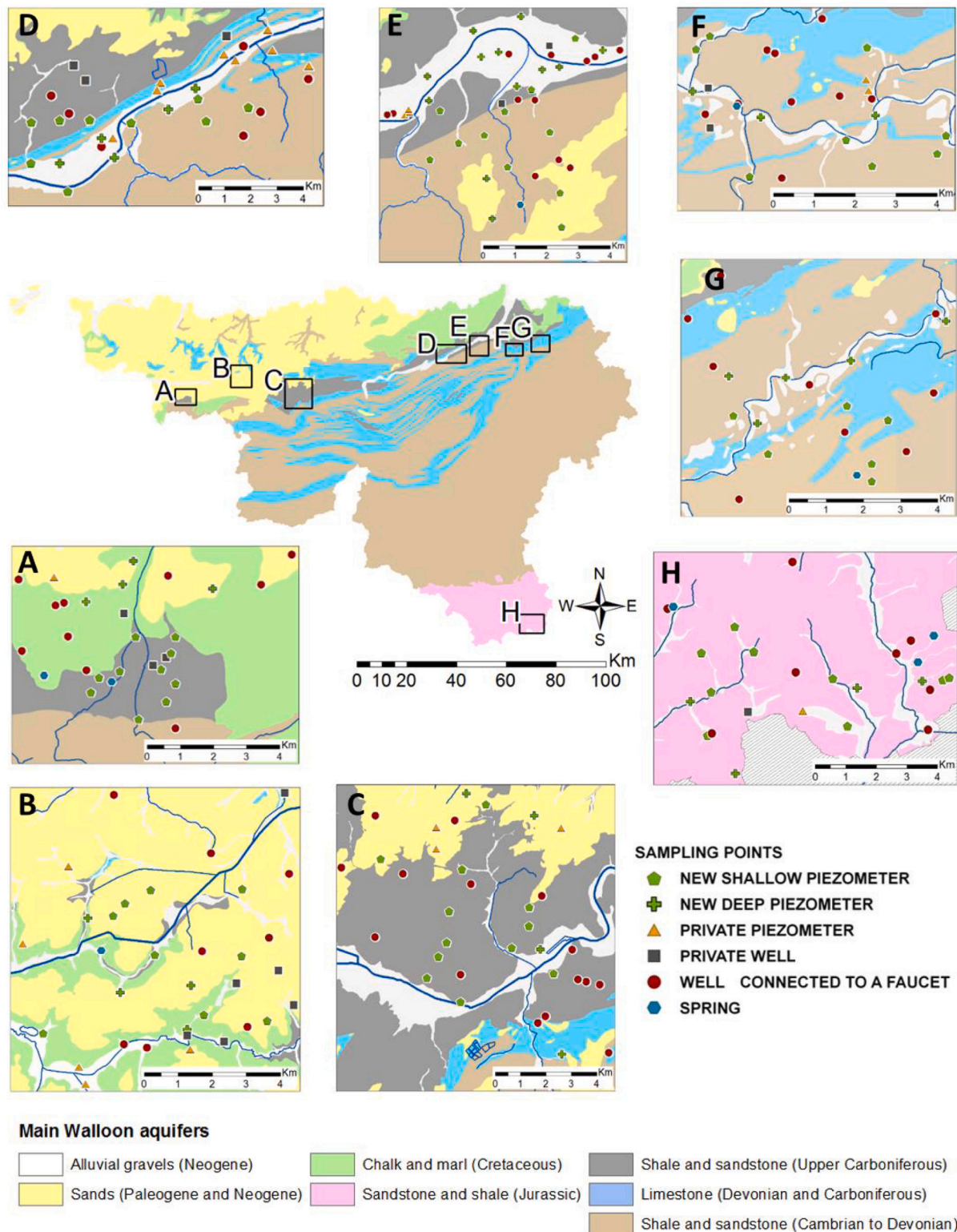


Fig. 2. : Main Walloon aquifers, zoom on the 8 areas (A-G) of investigation in urban and industrial context and sampling points types and location (from SPW - DGO3 - DGARNE, 2015a; SPW - DGO3, 2014, modified).

inhabitants, respectively, in 2020 (<https://www.citypopulation.de/en/belgium/agglo/>). The extreme South of Belgium, on the border of France and Luxembourg, is also an old industrial area.

The Walloon industry developed significantly during the 19th century. It was dominated by metallurgy (steelworks and zinc and lead extraction) and coal (extraction and blast furnaces). Other minor

industrial areas included, among others, quarries, glass and textile industry. The decline of these industries was initiated early in the 20th century. Currently, the industry is more diversified and specialized. The main industries always concern metallurgy but also chemical, pharmaceutical, power generation industrial activities (Boveroux et al., 2004). Coal is no longer extracted but many big coal heaps impact the

landscape and the old mining galleries are embedded in the upper Carboniferous geological layers.

From a geological point of view, three main contexts are distinguished: 1) Sambre, Meuse and Vesdre basins, 2) Haine basin and 3) southern Belgium. In Fig. 2, geological units are grouped into main aquifers, per age and lithology. More information on the main hydrogeological contexts of the region can be found in [Dassargues and Walraevens \(2014\)](#).

The Sambre, Meuse and Vesdre rivers are located along a major European set of aligned faults. The bedrock is composed of a succession of limestone, sandstone and shale, dated from Devonian to Carboniferous ages, the main one being the Upper-Carboniferous shale and sandstone formation containing coal and pyrite. Floodplains can reach a width of 3.5 km. The general groundwater flows occur along the direction of the floodplains, the alluvial aquifers being generally drained by the rivers. Devonian detrital formations and Upper Carboniferous shale and sandstone formations form aquitards. In these contexts, groundwater is located in the upper fringe of the altered rocks and the direction of groundwater flow is mainly governed by topography. Along the Meuse River, old terraces are locally confounded with local deposits of Eocene and Oligocene sands that overlie the bedrock. Sand deposits and old terraces generally contain superficial aquifers ([Dassargues et al., 2014](#); [Ruthy et al., 2014](#)).

In the valley of the Haine River, to the west, the bedrock is overlain by Meso-Cenozoic formations. Marl and chalk of upper Cretaceous and clays and sands of Paleocene and Eocene form a sedimentary basin, whose thickness can reach 150 m. Pleistocene and Holocene colluvium and alluvial sediments are in the valley bottoms. Pleistocene wind deposits, consisting of silt, locally cover the top of the slopes. Groundwater flows are directed to the Haine River ([Rorive and Goderniaux, 2014](#)).

In southern Belgium, the geological structure is typical of the Paris Basin (Triassic to Pliocene ages), consisting of a succession of monoclinal geological layers with south dipping. Sedimentary aquifer and aquiclude layers alternate, consisting of sandstone, marl and limestone. The thickness of each hydrogeological unit exceeds thirty meters. Groundwater flows are directed to the south along the layers inclination, but surface water locally drains groundwater to south-west or to south-east ([Debbaut and Bouezmarni, 2014](#)).

3. Materials and methods

3.1. Preliminary analysis of the data set

Existing groundwater analyses available for the whole region, to the exclusion of urban and industrial areas, were compiled from several databases, for comparison with new data collected in the urban and industrial areas. The selection and aggregation criteria for these chemical data were based on the most recent recommendations, particularly the proposals of the European project FP6 « BRIDGE » ([Müller, 2006](#)). Values smaller than detection limits were replaced by half the detection limit, as recommended in the BRIDGE project.

The dataset contains 70,870 records of inorganic trace elements analyzed on 7418 samples that come from 1965 sampling points located in all aquifers of the Region. The 1965 available sampling locations were grouped into 1432 sites. A site is here defined as a group of sampling points intercepting the same main aquifer in a same hydrogeological context and located within a distance of 600 m from each other. A single groundwater composition is attributed to each site: the median value is calculated per element and per site from all the analyses, even when multiple analyses were performed at the same point at different times.

3.2. Sampling network and analysis procedure

Eight areas representative of the different urban and industrial contexts of the Walloon region of Belgium were selected (Fig. 2), with two areas located in the Haine valley, one in the Sambre valley, two in

the Meuse valley, two in the Vesdre valley and one in the South of Belgium.

Sampling locations include existing wells (79), piezometers (40) and springs (9), but also new shallow (74) and deep piezometers (41) specifically drilled for the project in areas where existing sampling points were not available. Several criteria were considered for the selection of existing wells, piezometers and springs: (1) every hydrogeological unit was sampled; (2) groundwater samples were collected from the first encountered aquifer, usually at shallow depth; (3) using information and databases on polluted sites in the investigated areas, local pollutions were avoided. The main aquifers sampled in the urban and industrial areas are alluvial gravels (46 sampling locations), sands (27 sampling locations), Cretaceous chalk and marl (27 sampling locations), Jurassic sandstone and shale (26 sampling locations), Upper Carboniferous shale and sandstone (48 sampling locations), Carboniferous and Devonian limestone (23 sampling locations) and Devonian to Cambrian shale and sandstone (46 sampling locations).

The sampling campaign was performed from June 2010 to August 2011. Each groundwater sample was analyzed for 19 inorganic trace elements (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se and Zn), 59 organic micro-pollutants (16 polycyclic aromatic hydrocarbons, 8 monocyclic aromatic hydrocarbons, 18 halogenated volatile organic compound, 4 fractions of petroleum hydrocarbons and 13 chlorobenzenes, detailed list in Supplementary Material Nb 1) and 8 major and minor elements (Ca^{2+} , Mg^{2+} , HCO_3^- , NO_3^- , SO_4^{2-} , Cl^- , K^+ and Na^+). Samples for inorganic trace elements were filtered at 0.45 μm . Five physico-chemical parameters (pH, temperature, electrical conductivity, redox potential and dissolved oxygen) were measured in the field, in a flow-cell, at the time of sampling to determine the environmental conditions prevailing in groundwater.

Temperature, pH, redox potential and dissolved oxygen were determined in situ by potentiometry. The electrical conductivity was measured in situ by a conductivity meter. Calcium concentrations and alkalinity were obtained by potentiometric titration in the laboratory. Concentrations of major elements (Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and NO_3^-) were obtained by capillary electrophoresis. Most inorganic trace elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Mercury concentrations were determined by atomic absorption spectrometry with cold vapor (CV-AAS). Total chromium concentrations were obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Iron and manganese concentrations were obtained by atomic absorption spectrometry. BTEX, styrene and HVOC concentrations were obtained by gas chromatography coupled to mass spectrometry with static headspace (HS-GCMS). Non-halogenated polycyclic aromatic hydrocarbons (PAH) concentrations were determined by high-performance liquid chromatography (HPLC). Petroleum hydrocarbons were analyzed by gas chromatography coupled with a flame ionization detector (GC-FID). Chlorobenzene concentrations were obtained by gas chromatography coupled to mass spectrometry with static headspace (HS-GCMS) or coupled to an electron-capture detector (GC-ECD) according to the compound.

3.3. Statistical description and graphical representation of the data

Data are first described by main statistical values: mean, median and different percentiles. Distribution function plots are one of the most informative graphical displays of geochemical distributions ([Reimann and Garrett, 2005](#); [Reimann et al., 2005](#)). The shape of the curve may reflect the presence of various geochemical processes influencing the concentrations in water, such as redox reactions, adsorption - desorption reactions and mineral solubility – precipitation ([Shand et al., 2007](#)). Inflections or break points indicate the presence of multiple populations and outliers ([Sinclair, 1974](#)). Cumulative distribution functions are used here to plot the distribution because they have the advantage of not compressing the central part of the data range. The y-axis shows the cumulative probability of the distribution function between 0 and 1. The

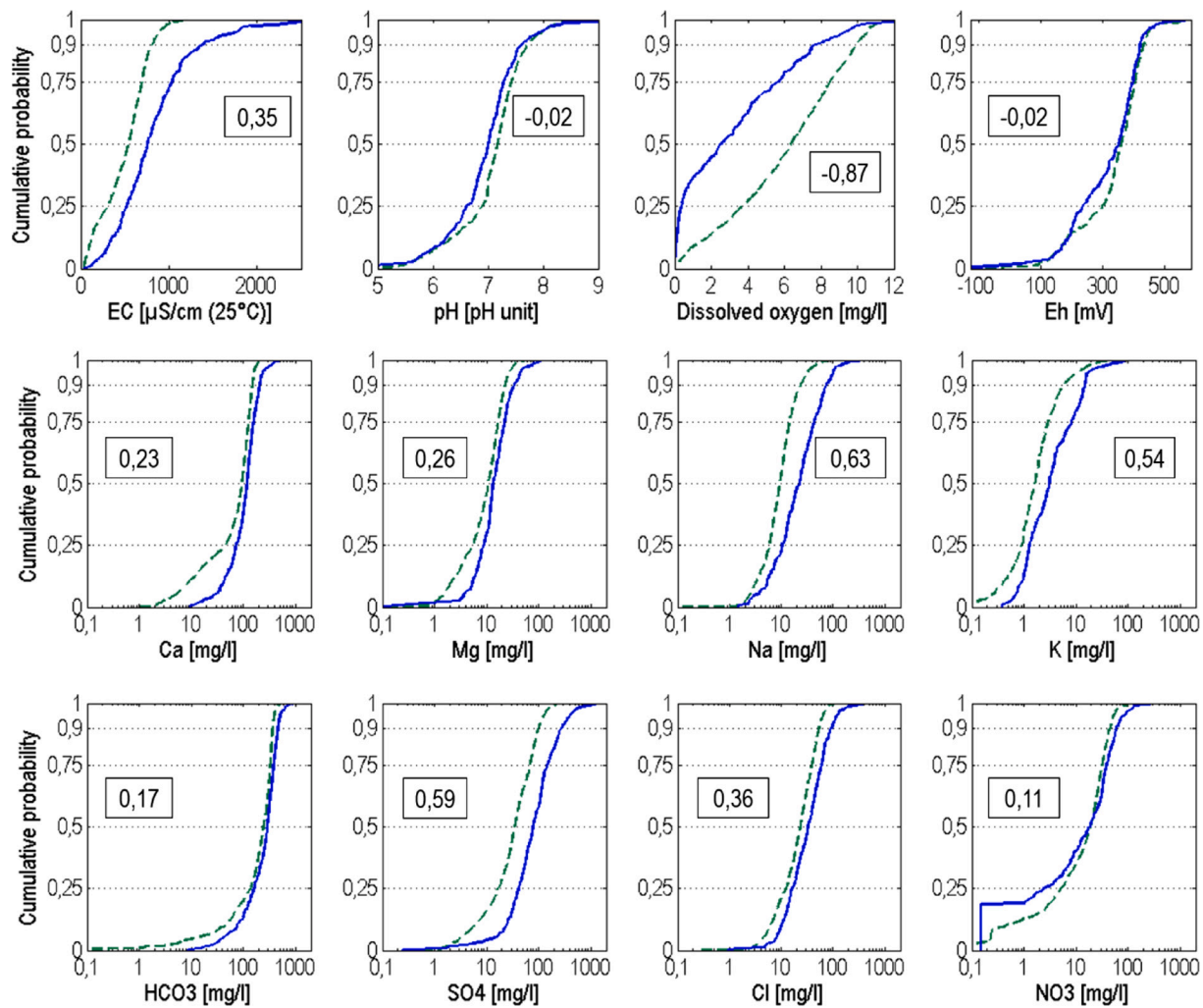


Fig. 3. : Comparison of the distribution (CDFPs) of physico-chemical parameters and major inorganic elements in the urban and the industrial areas (blue line) and in the entire Wallonia outside these areas (dashed green line). The calculated indicator of impact (I^2U) is noted in the box. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

x-axis shows values of concentration on a log-scale, because of right skewed distributions.

Cumulative distribution function plots (CDFPs) allow comparing the distributions of inorganic trace elements in urban and industrial areas (UIS) to those obtained in the entire Wallonia outside these areas (W). Because it is difficult to objectively compare different pollutants with different natural background and concentration levels in groundwater, we suggest to compute an indicator reflecting as much as possible the impact of inorganic trace elements of diffuse pollution in urban and industrial areas (Indicator of the Impact of Urban and industrial areas – I^2U). The distribution curves are sometimes disturbed by the detection limits achieved. Therefore, the indicator is based on the comparison of medians (sometimes influenced by the detection limits) and on the comparison of 90th percentiles (not influenced by the detection limits for the elements considered). The indicator used to classify the elements from most affected to least affected is calculated according to the Eq. (1). The greater the coefficient, the greater the impact of urban and industrial contamination on inorganic trace elements concentrations. CDFPs are also used to plot the distribution of major elements, of physico-chemical parameters and to compare the distribution of inorganic trace elements in the different lithologies, in urban and industrial contexts. An indicator equivalent to I^2U is calculated to quantify the influence of lithology on concentrations in groundwater. This indicator, named I^2L (Indicator of the Influence of Lithology), is calculated

according to the Eq. (2). The indicator is based on the comparison of medians calculated by lithology and on the comparison of 90th percentiles calculated by lithology.

$$I2U = \left[\left(\frac{med_{UIS} - med_w}{med_{UIS}} \right) + \left(\frac{P90_{UIS} - P90_w}{P90_{UIS}} \right) \right] / 2 \quad (1)$$

$$I2L = \left[\left(\frac{med_{max} - med_{min}}{med_{max}} \right) + \left(\frac{P90_{max} - P90_{min}}{P90_{max}} \right) \right] / 2 \quad (2)$$

Moreover, correlation coefficients were calculated for each pair of inorganic trace elements. Correlation coefficients were also calculated between inorganic trace elements and major ions or physico-chemical parameters measured during sampling operations. Correlation coefficients are determined to highlight chemical compounds with a similar behavior and the physico-chemical parameters affecting element mobility. The Kendall-tau method (Kendall, 1938) is used because data distributions of most parameters are skewed. Correlations are considered as non-significant when the p -value is greater than 0.001.

3.4. Determination of background concentrations for inorganic trace elements per main aquifer

Background concentrations have been determined in urban and industrial areas, taking into consideration the hydrogeological context.

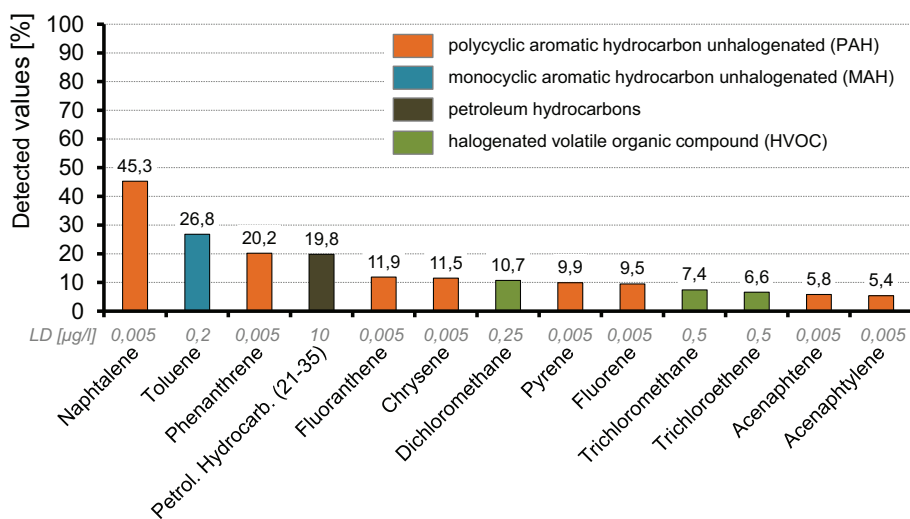


Fig. 4. : Frequency of detection (%) and limits of detection (LD) for the organic compounds. Only compounds detected in at least in 5% of the collected groundwater samples are represented.

The 90th percentile of the concentration distribution is selected as the background value, as advised by European guidelines (Müller, 2006).

4. Results and discussion

4.1. Hydrochemical characterization of the investigated areas

The general environmental conditions prevailing in groundwater can be described using the physico-chemical parameters measured in the field (Fig. 3). In urban and industrial areas, pH values are symmetrically distributed and close to neutrality (median: 7.02). The median of electrical conductivity values is 761 $\mu\text{S/cm}$ (at 25 °C). Half of the values range between 519 $\mu\text{S/cm}$ (1st quartile) and 1032 $\mu\text{S/cm}$ (3rd quartile). Measured redox potentials range between -128 mV (highly reducing conditions) and 585 mV (strongly oxidizing conditions). Half of the values are between 237 mV (1st quartile) and 398 mV (3rd quartile). Half of the dissolved oxygen concentrations are between 0.40 mg/l (1st quartile) and 5.72 mg/l (3rd quartile). Water temperature is generally around 12 °C, the usual temperature of groundwater in Belgium. The environmental conditions are more acidic and more reductive in urban and industrial areas than in natural areas and the electrical conductivity is higher in urban and industrial areas.

As expected in the Piper diagram (Piper, 1944), the dominant cationic form is calcium and the dominant anionic form is bicarbonate (Supplementary Material Nb 2). However, several groundwater samples show significant proportions of sulfate. Few samples also show large

proportions of Cl^- or NO_3^- , indicative of anthropogenic influence on groundwater composition.

Cumulative distribution function plots (CDFPs) are plotted for major elements to show the range of concentrations and to compare the distributions between the different chemical compounds (Fig. 3). The concentrations in major elements are generally higher in urban and industrial areas (blue line) than in natural areas (dashed green line), particularly for sulfate, sodium and potassium. CDFPs for sodium, potassium, chloride and sulfate show a large range of concentrations, over two orders of magnitude. Impact of pollution on their concentrations is evident (Shand et al., 2007). CDFPs for nitrate shows a strong negative skew, particularly in urban and industrial areas. This is probably the consequence of denitrification related to more reducing subsurface environments. CDFPs for calcium, magnesium and bicarbonate also show a slight negative skew. In these cases, the low concentrations can be associated with lower carbonate contents of the rock, short residence time or CO_2 degassing in the shallow part of the aquifer (Shand et al., 2007).

4.2. Occurrence of contaminants affecting groundwater in urban and industrial areas

This section summarizes the occurrence of organic and inorganic contaminants in the groundwater of selected urban and industrial sections of the Walloon Region. Concentrations of these compounds are compared with the regulations for drinking water set by WHO regulation

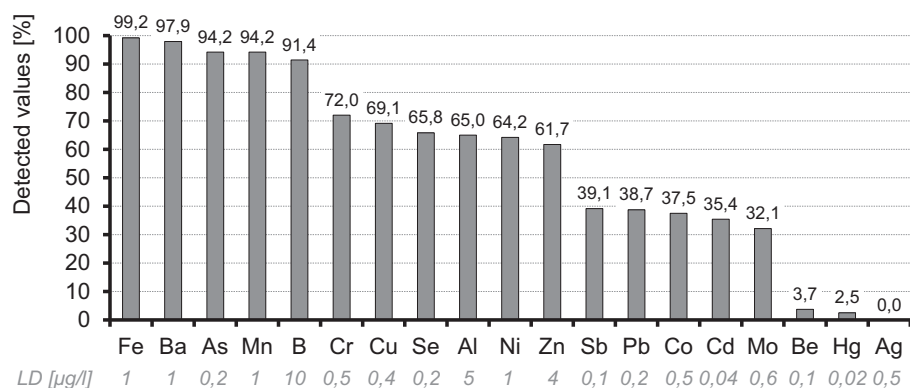


Fig. 5. : Frequency of detection (%) and limits of detection (LD) for inorganic trace elements.

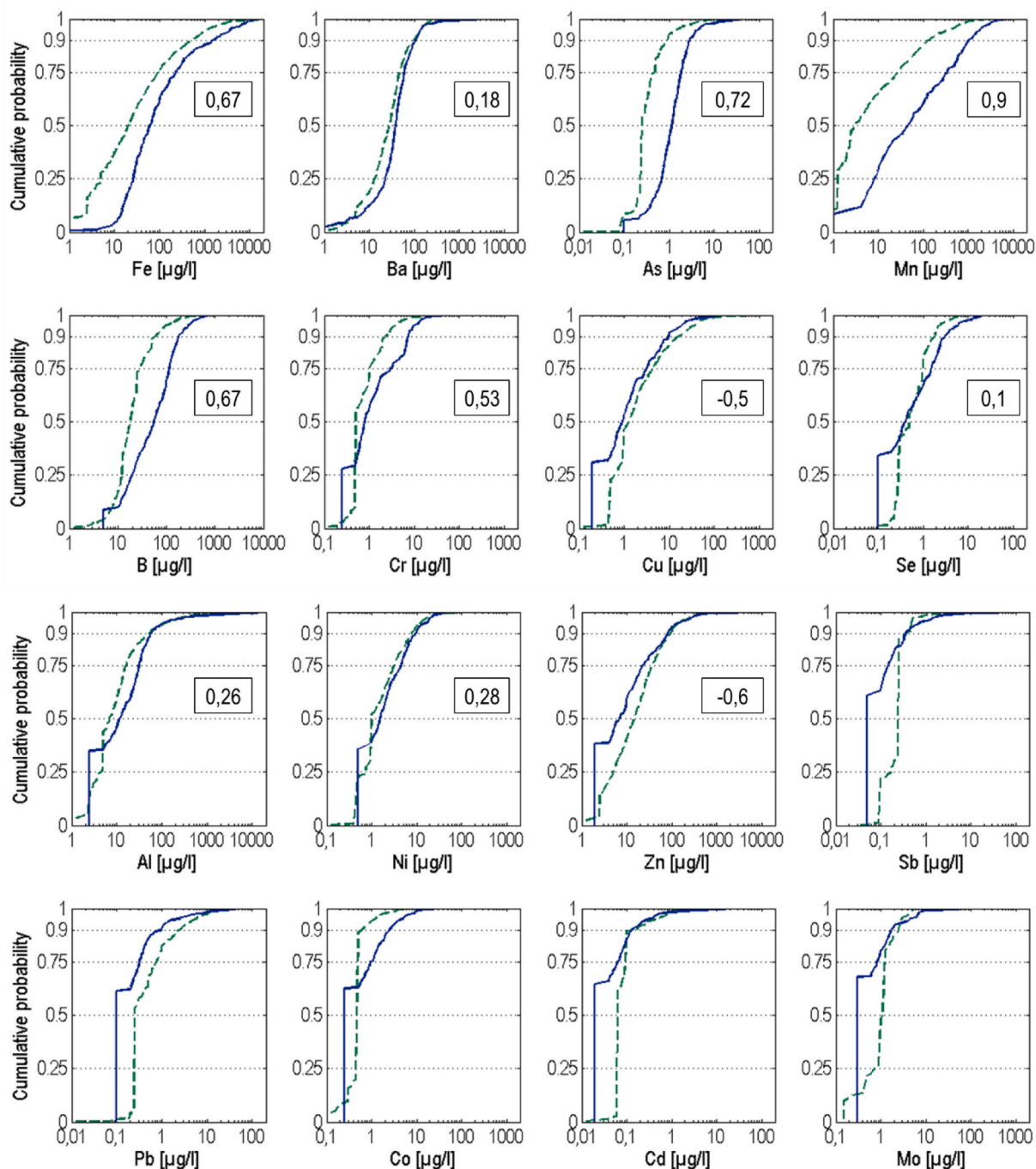


Fig. 6. Comparison of the distribution (CDFs) of inorganic trace elements in the urban and industrial areas (blue line) and in the entire Wallonia outside these areas (dashed green line). The calculated indicator of impact (I^2U) is indicated in the box (calculation of I^2U for Sb, Pb, Co, Cd and Mo was not possible because of their low detection level). Inorganic elements are ranked from largest to smallest percentage of detection in urban and industrial areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(WHO, 2017).

4.2.1. Concentrations of organic contaminants

Organic contaminants have been rarely detected in the investigated areas and CDFs were meaningless for these compounds. As an alternative, Fig. 4 shows the percentages of detection of the most often detected organic compounds. Supplementary Material Nb 1 provides a list of all the organic compounds analyzed and the respective percentages of detection. The concentrations at which organic contaminants were detected are below their solubility in groundwater. Naphthalene and phenanthrene are the most often detected PAHs in the dataset with

90th percentile of 0.1 $\mu\text{g/l}$ and 0.03 $\mu\text{g/l}$, respectively. Because of their molecular properties, they are more soluble and less adsorbed than other PAHs. Surprisingly, the heavier fraction of petroleum hydrocarbons is observed more frequently than the lighter fraction in the data set. The explanation is most probably related to the fact that lighter compounds are more bioavailable and readily degraded than heavier compounds. Toluene is the most found monocyclic aromatic halogenated hydrocarbons (MAHs) at 90th percentile of 0.61 $\mu\text{g/l}$. Finally, dichloromethane is the most often detected halogenated volatile organic compound (HVOC) at 90th percentile of 0.26 $\mu\text{g/l}$.

When considering the 90th percentile of concentrations of these

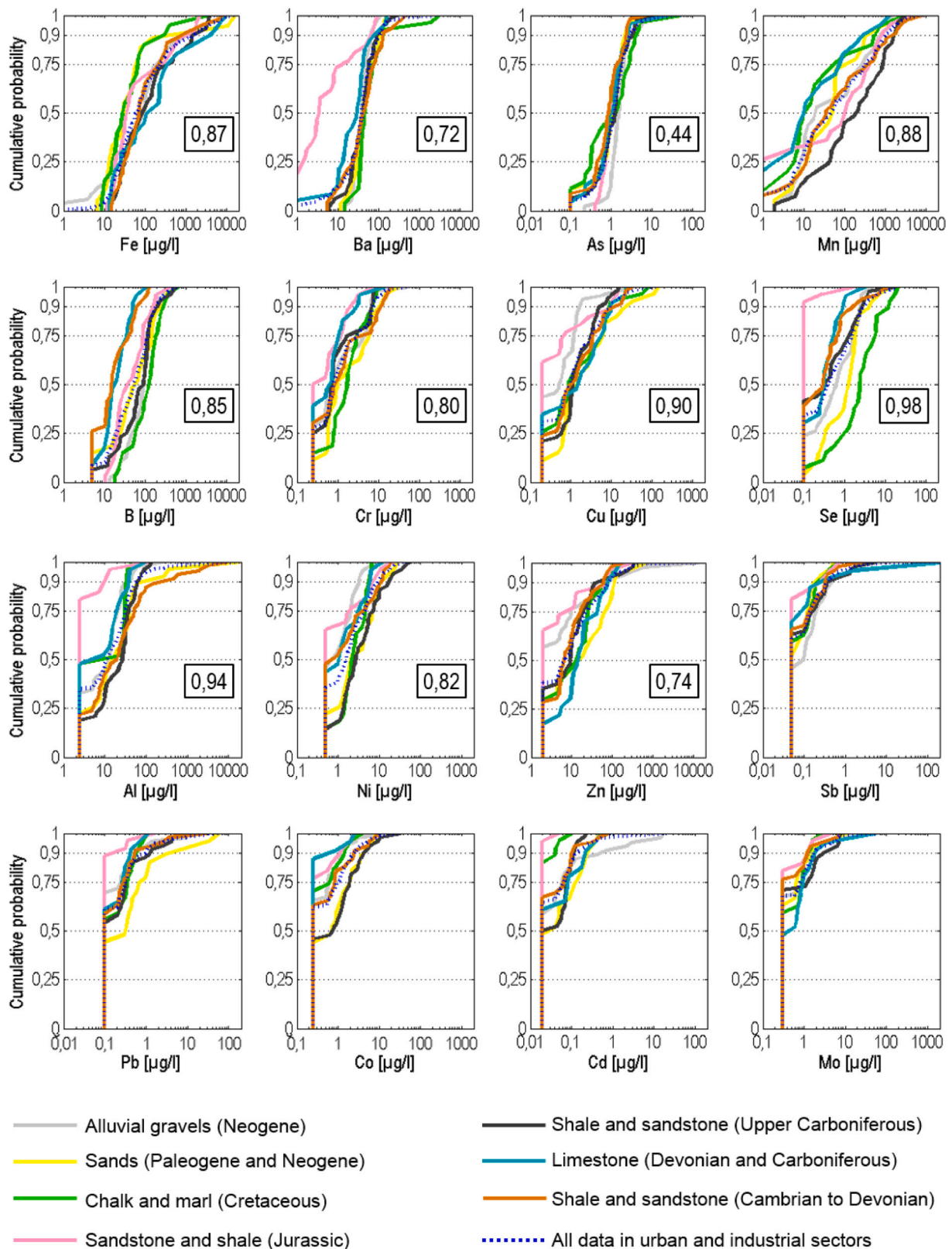


Fig. 7. Comparison of the distribution (CDFPs) of inorganic trace elements in the urban and industrial areas per main aquifer and for all data. The calculated indicator of the influence of lithology on concentrations in groundwater (I^2L) is indicated in the box (calculation of I^2L for Sb, Pb, Co, Cd and Mo was not possible because of their low detection level). Inorganic elements are ranked from largest to smallest percentage of detection in urban and industrial areas.

Table 1

Background concentration ($\mu\text{g/l}$) for each inorganic trace element, calculated from new data in the urban and industrial areas, per main aquifer. Values in bold italic correspond to the detection limit.

	Fe	Ba	As	Mn	B	Cr	Cu	Se	Al	Ni	Zn	Sb	Pb	Co	Cd	Mo
Alluvial gravels (Neogene)	1124	66.0	2.57	807	185	6.80	1.70	2.50	37.5	3.25	70.4	0.43	0.43	1.25	0.09	1.68
Sands (Paleogene and Neogene)	112	118	2.30	460	262	11.08	25.6	4.16	53.5	15.2	114	0.20	1.07	4.32	0.25	1.68
Chalk and marl (Cretaceous)	313	111	3.75	591	290	7.32	10.0	12.4	34.0	5.62	70.2	0.24	0.59	1.48	0.04	1.32
Sandstone and shale (Jurassic)	1306	67.5	2.95	875	180	2.20	9.70	0.20	10.0	8.70	72.5	0.26	0.21	1.15	0.04	1.25
Shale and sandstone (Upper Carboniferous)	1774	91.4	2.88	1710	206	7.20	5.75	2.86	64.3	19.0	47.6	0.35	0.46	3.90	0.12	3.25
Limestone (Devonian and Carboniferous)	4325	85.6	2.40	744	50.8	3.20	9.68	1.07	34.8	6.00	80.0	0.28	0.41	0.79	0.29	1.60
Shale and sandstone (Cambrian to Devonian)	886	118	2.40	1670	66.5	12.0	13.9	1.75	87.8	11.5	61.5	0.35	0.47	2.50	0.11	1.30

organic compounds, none of them exceeded the WHO drinking water guidelines (WHO, 2017).

4.2.2. Concentrations of inorganic trace elements

Fig. 5 shows the percentages of detection for inorganic trace elements. The most detected elements are iron, barium, arsenic, manganese and boron (more than 90% of detection rate) at median concentrations of 62, 40, 1.20, 48 and 56 $\mu\text{g/l}$, respectively. Chromium, copper, selenium, aluminum, nickel and zinc are often detected (more than 60% of detection rate) at median concentration lower than 12 $\mu\text{g/l}$. Antimony, lead, cobalt, cadmium and molybdenum show values below the detection limit for more than half of the analyses (respectively less than 40%, 39%, 38%, 36% and 33% of detection rate). Beryllium and mercury are rarely detected (less than 4% of detection rate). Silver is never detected. Consequently, beryllium, mercury and silver will not be considered further in the descriptions and interpretations. Among these metals, only the 75th and 90th percentile of concentrations for iron and manganese exceed the threshold values considered in Wallonia for the implementation of the EU groundwater directive or the limits established by the WHO for drinking water (Supplementary Material Nb 1).

Fig. 6 shows the CDFPs for the studied inorganic trace elements in the industrial and urban areas (blue line) compared to data outside these areas (dashed green line). Despite the large differences in the detection range, the different inorganic trace elements show very contrasted ranges of concentrations, with narrow distributions for elements such as arsenic, boron, chromium, selenium or nickel (concentrations ranging over less than 2 orders of magnitude) and large distributions for iron, barium, manganese, aluminum, zinc or antimony (concentrations ranging over more than 3 orders of magnitude). The main statistical values (mean, median, 25th, 75th and 90th percentile) can be deduced from these graphs and are compiled in Supplementary Material Nb 3.

Compared to the rest of the Walloon region, urban and industrial areas show strongly higher concentrations for manganese, arsenic, iron, boron and chromium ($I^2U = 0.90$ to 0.53). Nickel, aluminum, barium and selenium concentrations show slightly higher concentrations in urban and industrial areas ($I^2U = 0.28$ to 0.10). Copper and zinc show moderately lower concentrations in urban and industrial areas ($I^2U = -0.5$ to -0.6). For antimony, lead, cobalt, cadmium and molybdenum, more than half of the values in urban and industrial areas are below the detection limit and the I^2U indicator is not calculated. For these elements, the comparison can be based on the 90th percentile. This indicates that cadmium, molybdenum and antimony show similar concentrations within and outside the urban and industrial areas. Lead concentrations appear lower in the urban and industrial areas while cobalt concentrations are higher.

Fig. 7 allows comparing the CDFPs drawn per main aquifer for the studied inorganic trace elements. Most elements show contrasted concentrations depending on lithology. This is particularly the case for selenium ($I^2L = 0.98$), but also for aluminum and copper ($I^2L = 0.94$ and 0.90). Other elements show more similar concentration distributions regardless of the geological context. This is particularly the case for arsenic ($I^2L = 0.44$).

In addition, results obtained in the investigated urban and industrial areas were used to calculate background concentrations per inorganic trace elements and per main aquifer (Table 1) based on 90th percentile.

4.3. Discussion on factors controlling the occurrence of inorganic trace elements in groundwater

Inorganic trace elements are natural constituents of soil, rocks and groundwater. In addition, in urban and industrial areas, the amount of emitted pollutants is potentially high. This is especially true for inorganic trace elements in areas subject for many years to metallurgy and exploitation of metals deposits. Nevertheless, the mobility and dissolution of such elements remains dependent on environmental conditions such as redox conditions and pH. Therefore, the presence of inorganic trace elements in groundwater can be influenced by 3 factors: (F1) their emissions in the environment caused by industrial or urban activities, (F2) the geological context and (F3) environmental conditions prevailing in groundwater (especially pH and Eh) that are dependent on hydrogeochemical conditions in the environment, but can potentially be affected by urban and industrial activities. These factors may occur simultaneously and explain the occurrence of inorganic trace elements in groundwater.

The potential influence of anthropogenic emissions (F1) can be examined first by comparing concentrations within and outside urban and industrial areas (Fig. 6). The influence of geology (F2) can be examined by comparing concentration distributions between different geological contexts (Fig. 7). And finally, the influence of environmental conditions prevailing in groundwater (F3) can be examined based on correlation coefficients between chemical compounds (Table 2).

Manganese, arsenic and iron are the elements for which the effect of urban and industrial areas on concentrations is most pronounced (F1). These elements are well correlated. They are highly negatively correlated with the oxidation-reduction potential Eh and dissolved oxygen content (O₂diss). In addition, manganese is inversely correlated with pH, with the highest concentrations being found where the conditions are most acidic. Consequently, the environmental conditions (F3) play a decisive role in the presence of these metals in dissolved form, the highest concentrations being found in the presence of reducing or even acidic conditions. Indeed, in oxidizing conditions, iron and manganese form complexes with oxides and hydroxides and with organic matter, and precipitate. Arsenic is then adsorbed or co-precipitated with iron or manganese oxides and oxy-hydroxides (Dzomback and Morel, 1990). Correlation between arsenic and sulfate also suggests that arsenic originates from the oxidation of sulfide minerals (e.g. pyrite and arsenopyrite) by oxygen or nitrate. As has already been shown in other contexts (e.g. Pauwels et al., 2010; Lazareva et al., 2015), the presence of arsenic in solution is linked to a succession of several processes: oxidation of sulfide minerals, adsorption on manganese and iron oxy-hydroxides subsequently dissolved in a more reducing environment. In the data set, arsenic concentrations are similar regardless of lithology (F2), arsenic having the lowest I^2L value of all inorganic trace elements.

The effect of urban and industrial areas is also marked on boron

Table 2

: Correlation coefficients for the pairs of inorganic trace elements. Correlation coefficients for inorganic trace elements with physico-chemical parameters and with major elements. Only significant correlations are displayed (p-value <0.001). The higher the correlation, the darker the frame. EC = electrical conductivity. Inorganic elements are ranked from largest to smallest percentage of detected values.

	Fe	Ba	As	Mn	B	Cr	Cu	Se	Al	Ni	Zn	Sb	Pb	Co	Cd	Mo
Fe	Fe															
Ba		Ba														
As	0,24		As													
Mn	0,33		0,29	Mn												
B			0,27		B											
Cr						Cr										
Cu							0,16	Cu								
Se	-0,17	0,16		-0,17	0,21	0,16		Se								
Al		0,17							Al							
Ni				0,22			0,18			Ni						
Zn							0,45		0,19	Zn						
Sb			0,31		0,16			0,24		0,17		Sb				
Pb			-0,17			0,18	0,44						Pb			
Co	0,27	0,17							0,27	0,44		0,18		Co		
Cd							0,21			0,34	0,36	0,21		0,21	Cd	
Mo			0,29													Mo

O ₂ diss	-0,25		-0,20	-0,40										-0,21		
CE			0,29		0,37		0,21									
Eh	-0,26		-0,19	-0,27		0,19										
pH				-0,19				-0,23	-0,24					-0,20	-0,17	

Ca			0,31		0,31		0,21									
Mg			0,19		0,24		-0,16									
Na		0,21	0,15		0,39		0,30	0,17	0,15					0,16		
K		0,16	0,24		0,45		0,24		0,16	0,16	0,27					0,28
NH ₄																
Cl					0,23		0,16									
SO ₄			0,30	0,16			0,26		0,18					0,18		
NO ₃	-0,34			-0,36		0,23	0,45			0,16		0,18		-0,16		
HCO ₃			0,17		0,32											-0,20
SiO ₂			0,19						0,17							

levels (F1), probably caused by high boron concentrations in urban effluents, boron being used as a bleaching agent (Barth, 1998). Boron concentrations are also significantly correlated with the electrical conductivity measured in-situ and with the concentrations of most major elements. These correlations, coupled with a strong variation in

concentrations according to the lithology, indicate that boron must also have a geogenic origin (F2).

Zinc, copper and lead are significantly correlated. Contrarily to most of the other inorganic trace elements, although copper, lead and zinc are generally emitted in greater quantities in industrial contexts, they show

lower concentrations in urban and industrial areas than outside (F1). Copper shows significant correlation with the redox potential and the three elements are positively correlated with nitrate (F3). Sulfide oxidation coupled with nitrate reduction is probably one of the main processes responsible for high concentrations of these elements. The link between high nitrate concentrations and the presence of zinc has already been observed (Pauwels et al., 2010). The concentrations in the different lithologies are very different for copper, lead and zinc (F2).

Nickel, cobalt and aluminum are well correlated with the inverse of pH. Occurrence of slightly more acidic conditions appears to be the main factor favoring higher concentrations for these inorganic trace elements (F3). Nickel and cobalt are easily incorporated into or sorbed on Mn and Fe oxides and oxo-hydroxides and their presence in dissolved form in groundwater is partly related to the dissolution of these oxyhydroxides (Dzombak and Morel, 1990). Moreover, aluminum is amphoteric, soluble under acidic conditions ($\text{pH} < 5$) in the form of $\text{Al}(\text{III})$, but also in very alkaline conditions ($\text{pH} > 8.5$ rarely encountered in groundwater) (Hem, 1991). In the dataset, aluminum and nickel show high indicators (I^2L) of the influence of lithology on concentrations in groundwater (F2).

Selenium shows very contrasted concentrations depending on lithology (F2), with a significant correlation with in-situ electrical conductivity and with the concentrations of most major elements, mainly nitrate. These correlations, coupled with the large variation in concentrations per lithology, indicate that selenium has a geogenic origin. The strong correlation of selenium with nitrate and, to a lesser extent, with sulfate suggests that selenium is mainly dissolved in relation with the sulfide oxidation coupled to autotroph nitrate reduction (F3). The occurrence in groundwater of selenium under slightly reducing conditions, as well as the role of nitrate on selenium oxidation and dissolution have been reported already in other contexts (Bailey et al., 2012; Cary et al., 2014; Mast et al., 2014; Wright, 1999).

The effect of diffuse urban and industrial contamination on barium (F1) levels is not significant and barium does not seem sensitive to environmental conditions (F3). The geological context only has an impact on barium concentrations (F2).

The effect of urban and industrial areas is also marked on (total) chromium levels (F1), probably caused by dissolution of Mn and Fe oxyhydroxides containing co-precipitated chromium. Chromium concentrations are also very significantly different according to geological contexts (F2). However, no correlation is evident between chromium and other parameters.

5. Conclusions and perspectives

The composition of groundwater is altered in urban and industrial areas with increased levels of most organic contaminants and inorganic trace elements. Some organic contaminants are often detected in urban and industrial areas. The most frequently detected organic compounds are naphthalene, toluene, phenanthrene, the heavier fraction (21–35) of petroleum hydrocarbons, fluoranthene, chrysene, dichloromethane, pyrene, and fluorene.

Anthropogenic influence is not limited to inputs of inorganic pollutants. It also causes changes in environmental conditions prevailing in groundwater with, in general, significantly more reducing and slightly acidic conditions. This results in changes in the precipitation - dissolution of mineral phases (such as iron and manganese oxo-hydroxides or sulfide minerals) and to sorption - desorption and immobilization - mobilization of inorganic pollutants in groundwater. This seems to be the main factor responsible for high concentrations of manganese, arsenic and iron (mainly associated with more reducing conditions), and of nickel, aluminum and cobalt (mainly associated with slightly more acidic conditions). In contrast, copper, lead and zinc show lower concentrations in urban and industrial areas because the redox conditions are more reducing in these areas. Copper, lead and zinc are indeed more often observed in groundwater in slightly reducing (anaerobic) redox conditions, in association with the oxidation of sulfide and coupled to

the reduction of nitrate. Selenium is also more often observed in groundwater under the same environmental conditions. An indicator, I^2U , allow quantifying the impact on organic trace elements of diffuse pollution in urban and industrial areas. The influence of lithology is also marked in the data set. Most elements have contrasted concentrations depending on lithology, particularly selenium and aluminum, but not arsenic which is present in equivalent concentrations whatever the lithology. Another indicator, I^2L , allow quantifying the influence of lithology on concentrations in groundwater.

As a general conclusion, the results show that, regardless of any additional intake of inorganic pollutants related to industrial and urban activities, environmental conditions prevailing in groundwater have a determinant effect on the occurrence at higher (or lower) concentrations of many inorganic compounds in groundwater. However, such changes in environmental conditions may be the indirect consequence of the industrial and urban activities which are more prone to contaminate groundwater with organic compounds which biodegradation contributes to modifications in Eh and pH. Geological contexts and lithologies may also partially influence environmental conditions prevailing in groundwater. Therefore, the influence of environmental conditions is fundamental and the influence of the additional anthropogenic inputs is less pronounced.

Finally, background concentrations calculated per inorganic trace elements and per main aquifer, in the urban and industrial areas, allow considering the “ambient background” in site remediation decision procedures. In general, remediation objectives are established from threshold concentrations based on health and ecotoxicological standards and associated risks. In areas where regional background concentrations exceed those thresholds, there is no evidence that soil or groundwater degradation is the responsibility of the site owner and remediation objectives can be adapted to this regional context. Following this study, decision makers have useful data for determining remediation objectives adapted to the current context.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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