GEOLOGICA BELGICA (2010) 13/3: 257-268

INFLUENCE OF MAJOR ELEMENTS ON HEAVY METAL COMPOSITION OF RIVER SEDIMENTS

Valerie DE SAEDELEER[1], Valérie CAPPUYNS[1,2] , Ward DE COOMAN[3] & Rudy SWENNEN[2]

(4 figures, 6 tables)

[1]Hogeschool-Universiteit Brussel, Centrum voor Economie en Duurzaam Ondernemen, Stormstraat 2, 1000 Brussel. E-mail: valerie.cappuyns@hubrussel.be
[2]Katholieke Universiteit Leuven, Department of Earth and Environmental Sciences, Celestijnenlaan 200E, 3001 Heverlee
[3]Vlaamse Milieumaatschappij, DVP Waterbodemmeetnet, Dr. De Moorstraat 24-26, 9300 Aalst

ABSTRACT In the present study, the relationship between heavy metals (As, Cd, Cr, Cu, Hg, Pb, Ni, Sn and Zn) and major elements and the location and/geological substrate of 105 river sediments in Flanders was investigated. Factor Analysis was used to divide the dataset into four components: a first component including clay, organic matter, Na, Ca, K and Mg, a relationship between Fe, As and Cd, an anthropogenic factor (including Cu, Hg, Pb, Sn and Zn) and finally the pH and insoluble residue. Regression equations were constructed, using major elements such as Fe and Ca as independent variables, besides more classical explaining variables such as clay content (< 2μm fraction), organic matter content and pH. Most heavy metal concentrations could be predicted very well by the independent variables, except Zn, Se and Sn. The results from this study, performed on a dataset of 105 riverbed sediments, indicate that, besides organic matter and clay content, other variables such as the total Fe and Ca content can be relevant parameters to predict heavy metal concentrations in sediments. The more general applicability of the obtained regression equations should be verified, and the inclusion of Fe and Ca in regression equations that are applied for the standardization of total metal concentrations in soils and sediments, should be considered.

KEYWORDS: background value, heavy metals, multiple regression, river sediments

1. Introduction

1.1 Background concentration of trace metals in soils and sediments

Trace element concentrations in soils and sediments are mainly dependent on the nature of the parent material from which they are derived, but anthropogenic influences can also alter trace element concentrations in terrestrial and fluvial environments. Consequently the natural background concentration of trace elements in soils and sediments can be used as a reference value to estimate the contamination level of soils and sediments. In the past, quantitative relationships between the bedrock and the surrounding soil and/or sediments have been established by several authors (e.g. Sondag & Duchesne, 1987; Martinez-Cortizas, 2003; Neff et al., 2006), but further development of the soil, weathering, erosion and transportation processes can alter this relationship between the soil and the underlying lithology (Martinez-Cortizas, 2003; Marques et al., 2004; Salvador-Blanes et al., 2002).

The occurrence of background concentrations of trace elements in soils and sediments is, besides the lithology, also influenced by their clay and organic matter content (Tack et al., 1997; De Temmerman et al., 2003, Diez et al., 2007; Roca et al., 2008). Therefore, clay and organic matter content are often used to calculate ‘corrected’ background values for trace metal concentrations in soils and sediments. In an attempt to establish a regression model to explain trace element concentrations in Flemish soils, Tack et al. (1997) found a rather poor relationship between total heavy metal concentrations in soils and the clay- and organic matter content. This indicates that the independent variables (clay and organic matter content) are not sufficient to explain trace element concentrations in soil and that the addition of other variables could probably improve the model.

Besides clay-minerals, Fe-rich accessory minerals such as Fe-oxi/hydroxides and phylosilicates are often concentrated in the clay fraction (< 2μm) (Schulze, 1988). To overcome this drawback of the ‘clay fraction”, data normalization towards “conservative elements” (Al, Fe, Li …) is often carried out. In many studies, Fe and/or Al are used as ‘normalizer to account for the natural variability of trace elements in soils and sediments (Summers et al., 1996; Covelli & Fontolan, 1997). Despite the fact that Fe is sensitive to redox processes and that small proportions of Fe may be of anthropogenic origin, a positive linear relation between Fe and trace element concentrations has been found in several studies. Sterkeman et al. (2006) found a linear relationship between the total concentrations of As, Co, Mo, Ni and Pb and the Fe-content of soils from the Northern part of France. The latter authors showed that the fine textured soil were characterized by higher concentrations of Cd, Co, Cr, Cu, Ni and Zn in comparison with coarse-textured soils, resulting in a strong association of the total Co, Cr and Ni content with total concentrations of Fe and Al. In uncontaminated soils, developed on shale in the southern part of the Grand Duchy of Luxemburg, a linear relationship was also established between total Fe and As concentrations, indicating that total Fe-concentrations could be an important variable to take into account when reference values for As are established in these soils (Horckmans et al., 2004).

In Flanders (Belgium), The Flemish Decree on soil Remediation (VLAREBO, 2006), establishes reference values, target values, and remediation values for heavy metals and organic contaminants, taking into account the pH (KCl) of the soil in addition to the clay content and organic matter content, but not the content of major elements or so called conservative elements such as Fe, Ca, Al, Li.

Trace elements occur in concentrations of less that 1 % in soils and rocks and therefore, heavy metals are also classified as 'trace elements'. In the present study, the term 'heavy metals' will refer to As, Cd, Cu, Cr, Hg, Ni, Pb, Sn and Zn, although As, Se and Sn are no metals but metalloids with properties intermediate between metals and non-metals.

1.2 Trace elements in river sediments in Flanders

In Europe, stream sediments have widely been used as a sampling medium for geochemical mapping. Since 1985 the Forum of European Geological surveys (FOREGS, previously WEGS) has been working on a geochemical atlas of Western Europe to deduce background geochemical information and to assess environmental pollution of floodplain and present-day river systems (Bölviken et al., 1996). The proposed methodology makes use of overbank sediments, which are considered a representative sampling medium for geochemical mapping (Ottessen et al., 1989) and active stream sediments to assess present-day anthropogenic pollution. In Belgium and Luxembourg, a systematic sampling of overbank sediments according to the L-U-S sampling protocol (Bölviken et al., 1996,) was performed by Swennen et al. (1996, 1998) and Swennen & Van der Sluys (1998, 2002). 66 locations in Belgium and Luxembourg were sampled according to the L-U-S sampling protocol and analyzed for major and trace elements. L stands for the 'lower' overbank sediment sample taken at depth in an overbank sediment profile and is considered to reflect pre-industrial and often pre-anthropogenic sedimentation and thus also background geochemical characteristics. The upper (U-) overbank sediment sample taken within the upper 5 to 25 cm of an overbank sediment profile is supposed to reflect the background signature with superimposed anthropogenic influences and gives an assessment of actual degree of pollution of the floodplain. Finally, the bulk active stream (S-) sediment indicates present-day degree of pollution, superimposed on the background concentration.

The study of Swennen et al. (1996, 1998) revealed the existence of significant different background concentrations between the northern and the southern part of Belgium in relation to differences in geological substrate. In the north dominantly non-lithified Quaternary

Contaminants	Reference value	[1]X	[1]Y	[1]Z
Arsenic	11	27.5	69.3	173.8
Cadmium	0.38	1.0	2.4	6.0
Chromium	17	42.5	107.1	268.6
Copper	8	20.0	50.4	126.4
Mercury	0.05	0.1	0.3	0.8
Lead	14	35.0	88.2	221.2
Nickel	11	27.5	69.3	173.8
Zinc	67	167.5	422.1	1058.6
APHC	37	92.5	233.1	584.6
EOX	31	77.5	195.3	489.8
Sum OCP	3.9	9.8	24.6	61.6
Sum 7 PCB's	5.1	12.8	32.1	80.6
6 PAH's of Borneff	0.220	0.6	1.4	3.5

[1]Below x= category 1, between X and Y = Category 2, between Y and Z : category 3, above Z = category 4.

Table 1: Reference values for the different physico-chemical parameters and for the threshold values of the different categories (Flemish Environmental Agency, 2009.). APHC = apolar hydrocarbons, EOX = extractable halogenated organic compounds, OCP's = organochlorpesticides, PCB's = polychlorinated binfenyls, PAH's : polyaromatic hydrocarbons, DM = dry matter. All concentrations in mg/kg DM.

Log PTR	Enrichment	Category	Color	Deviation from reference
< 0.4	< 2.5	1	blue	No deviation
0.4-0.8	2.5-6.3	2	green	Small deviation
0.8-1.2	6.3-15.8	3	yellow	Deviation
> 1.2	> 15.8	4	red	Strong deviation

PTR : proportion to reference = measured value/reference value

Table 2. Physico-chemical categories (Flemish Environmental Agency, 2009.)

and Tertiary sands, marls and clays occur while in the south Palaeozoic sandstones, shales and carbonate rocks outcrop out, resulting in different background concentrations in the northern and the southern part of Belgium. The most important pollution was found in the northern part of Belgium because of the high population density and industrial activities over the last decades in that region.

Since 2000, the Flemish Environmental Agency (2009) is monitoring the sediment quality of 600 locations in Flanders in both navigable and unnavigable waters, according to the TRIADE approach. This TRIADE sediment quality assessment is an integrated investigation technique based on the analysis of physico-chemical, biological and ecotoxicological parameters (Chapman, 1990; De Cooman & Detemmerman, 2003). For the evaluation of the physico-chemical parameters, a standardization to an organic matter content of 5% and a clay content of 11% is performed for heavy metals and organic contaminants (De Cooman & Detemmerman, 2003; Leloup et al., 2007).

Depending on the enrichment of the contaminants (As, Cd, Cr, Cu, Hg, Pb, Se, Ni, Sn, Zn, polyclorbifenyls (PCB's), polycyclic aromatic hydrocarbons (PAH's), mineral oil en halogenated organic components) towards a reference value (Table 1), the sediments are divided into 4 categories, going from "no deviation from the reference (category 1), to "strong deviation from reference" (category 4) (Table 2).

The aim of the present study was to investigate the relationship between heavy metals (As, Cd, Cr, Cu, Hg, Pb, Ni, Sn and Zn) and major elements and the location and/geological substrate of 105 river sediments in Flanders. Therefore, in addition to the parameters mentioned in Table 1, major elements (Al, Ca, K, Mg and Fe) were analyzed in 105 representative sediment samples from the sediment monitoring network of the Flemish Environmental Agency. Aluminium is often used as a proxy for the clay content and therefore often included as a normalization factor in the determination of geochemical baselines (Covelli & Fontolan, 1997). In the present study, however, Al was not measured in the samples, but the clay content ($< 2\mu$m fraction) was determined.

2. Materials and methods

2.1 Sampling

For this study, 105 river sediments, sampled between March and June 2006 were provided by the Flemish Environmental Agency. The samples originated from 11 river basins: (The number between brackets gives the amount of sediment samples that were taken in the respective river catchment): Lower Scheldt (8), Upper

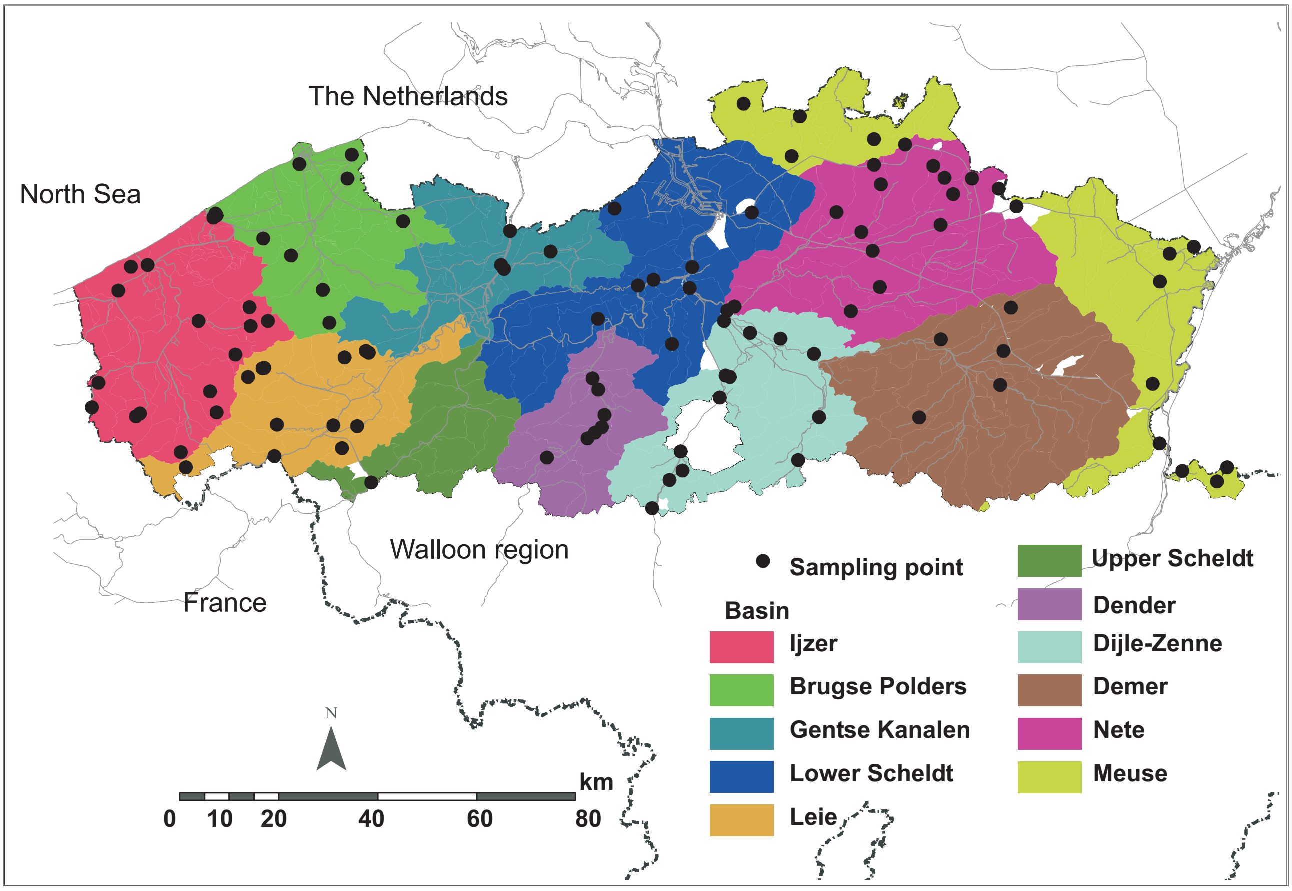

Figure 1. Location of the river basins and sampling points analyzed in this study.

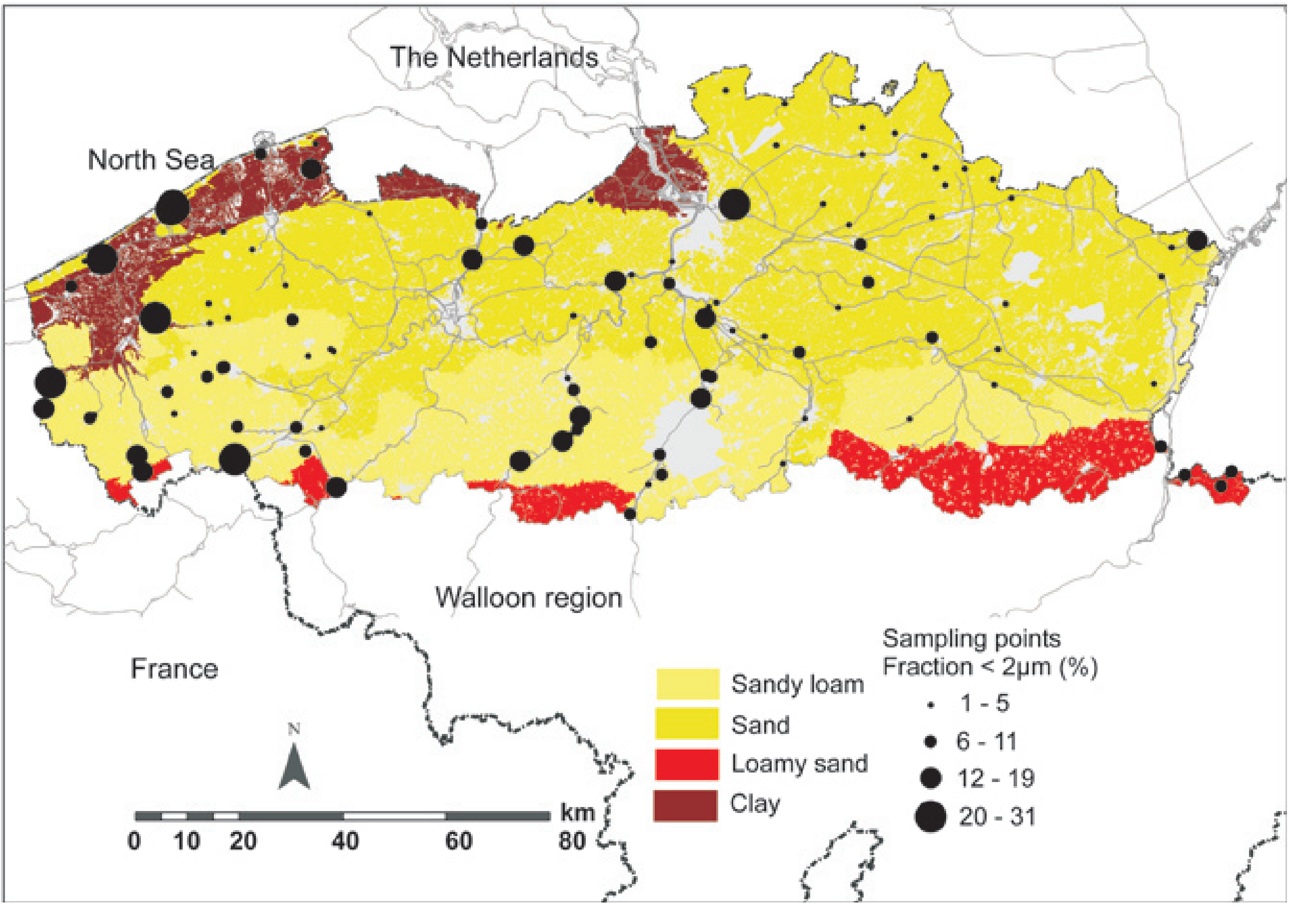

Figure 2. Location of the sampling points (dots) analyzed in this study, with indication of the dominant textural classes. The size of the dots gives an indication of the clay content (< 2μm fraction) of the sediments.

Scheldt (1), Brugse polders (11), Demer (5), Dender (7), Dijle-Zenne (14), Leie (13), Meuse (13), Nete (14), Gentse kanalen (4) and IJzer (15) (Fig. 1). On Fig. 2, the dominant soil textural classes are indicated, reflecting the variation in geological substrate in Flanders. The northern part of Flanders mainly consists of Quaternary sandy deposits, whereas the interior part of Flanders is mainly composed of Tertiary deposits. The sandy soils of the northern part of Flanders gradually change into loamy soils, forming a large sandy loam region. In the Polder region, the north-western part of Flanders, clayey soils are dominant (Fig. 2).

In each of the 105 sampling location, 20 subsamples of the river bed were taken at a depth of maximum 20 cm to obtain a composite sample of approximately 45 l. The composite sample was homogenized. Part of this sample was air-dried and sieved <2 mm before physico-chemical analysis, whereas another part was stored in a refrigerator in the dark to perform ecotoxicological and biological tests. In the present paper, attention will only be given to the results of the physico-chemical analysis of the river sediments.

The digitized geological map of Flanders (http://dov.be) was used to determine the geological substrate at selected sampling locations. The relationship with the geological substrate was only assessed in a qualitative way at selected locations.

2.2 Physico-chemical Analysis

Dry matter content of sediment samples was determined by drying them for 24 h at 105 °C. All the results of the sediment analysis are expressed as mg/kg dry matter or in weight%. pH(H_2O) was measured by directly inserting a pH-electrode in the wet sediment. The sand and silt content was determined by wet seeving (50 μm mesh seeve) on the < 2 mm fraction, after removal of coarse fragments and $CaCO_3$ (HCl-treatment) and Fe-(hydr) oxides (Na-oxalate treatment). For the < 2μm fraction (the “so-called” clay content), the method of Robinson-Khön (ISO standard 11277, 1998) was applied. The total organic carbon content was measured by infrared detection after oxidation of the organic carbon to CO_2 (Crompton, 2000).

Total element concentrations of major elements (Mg, Na, K, Ca and Fe) and Mn were determined after digestion of the sediment sample with a mixture of 4 strong acids. Therefore, one gram of each sample was dissolved in a 4-acid mixture (4 ml HCl_{conc}, 2 ml HNO_{3conc} 2, ml HF_{conc} and 2 ml $HClO_{4conc}$) in a Teflon beaker. The mixture was gently heated on a hot plate until half dry and subsequently reattacked with the same four acids and heated until completely dry. The residue was redissolved with 20 ml 2.5 N HCl and filtered (Whatman 45). Finally, the solution was diluted to 50 ml with distilled water. These solutions were analyzed by AAS (Varian® Techtron AA6). The final residue that remained after the treatments with the 4 concentrated acids was dried in an oven at 105°C and weighted to determine the insoluble residue (IR, expressed in mass %).

Total concentrations of As, Cd, Cr, P, Cu, Pb, Hg, Ni, Se, N, Sn en Zn were determined after aqua regia (3:1, v/v, HCl to HNO_3) digestion procedure (ISO standard 11466, 1995) by ICP-AES.

A certified reference material (GBW07411 Soil) and sample duplicates were used for quality control. Values (in mg/kg) obtained were for Cd 25.9 (certified value 28.2±1.3), Zn: 3630 (certified value 3800±300), Ni: 22.3 (certified value: 24.2±2.1), Cu: 62.9 (certified value 65.4±4.7), Pb: 3010 (certified value 2700±100), Cr: 57.5 (certified value: 59.6±5.0) and As: 193 (certified value 205±11). Relative standard deviations on triplicate analysis were below 5% for all elements, except Ca (below 10%). All reagents used for analysis were of analytical grade. All glassware was acid rinsed with HNO_3 0.2 M before usage.

2.3 Statistical analysis

Statistical analysis was performed with the software package SPSS 15.0 for Windows. Descriptive statistics (average, median, minimum, maximum, standard deviation and variance) were calculated for each variable. The normal distribution of the variables was checked by means of the Kolomogorof-Smirnov (K-S) - test and correlations between variables were tested by calculating two-tailed Pearson correlation coefficients for the log-transformed values. Analyze of variances (ANOVA) was applied to compare averages of the variables between river basins. Factor Analysis was performed to gain a better insight in the relationship between variables. Factor analysis and Principal Component Analysis (PCA) have been used by many authors (e.g. Mico et al., 2006; Salonen & Korkka-Niemi., 2007; Zhao et al., 2007) for the interpretation of environmental data and to distinguish natural and antropogenic values of trace elements in the environment. Finally, multiple linear regression was performed to deduce possible causal relationships between the variables. Attention was mainly paid to the possibility of predicting trace element concentrations in sediments based on major element composition, pH, clay- and organic matter content.

For the statistical analysis, the recommendations of Webster (1997, 2001) (reporting mean values with standard errors, performing linear regressions, etc.) were taken into account.

3. Results and discussion

3.1 Descriptive statistics

In the dataset, only dry matter content, pH, temperature, oxygen content and K possess a normal distribution (Table 3). As, Cd, Cr, Cu, Hg, Pb, Ni, Se, Sn, Zn, organic matter (OM), clay, P, N, Ca, Fe, Mg, Mn, Na and IR showed a significance of less than 0.10 in the K-S test. Therefore, all the variables except pH were logtransformed.

Average trace metal concentrations decreased according to: Zn > Mn > Pb > Cr > Cu > Ni > As > Sn > Se > Cd > Hg.

The construction of boxplots (Fig. 3) allows evaluating which of the observations could be considered as outliers.

Table 3. Descriptive statistics

Variable	Symbol	Unit	Mean	Median	Stdv	Min	Max	p-value K-S test
Clay		%	7.5	5.5	6.6	1	32	.008
Organic matter	OM	%	10.0	8.4	8.0	0	42	.006
Dry matter	DM	%	59.8	61.0	15.1	23	85	.328
pH	pH		7.7	7.7	0.5	6.5	9.2	.605
Oxygen	O_2	mg/l	8.2	8.5	3.6	0.4	17.0	.822
Temperature		°C	12.6	12.5	4.6	3.3	25.1	.908
Insoluble residue	I.R.	%	3.4	3.0	2.2	0.1	12.4	.107
Arsenic	As	mg/kg	9.7	8.0	8.5	1	61	.005
Cadmium	Cd	mg/kg	1.3	0.6	1.5	0.1	7.5	.000
Chromium	Cr	mg/kg	32.8	27.0	27.4	1.8	172	.048
Copper	Cu	mg/kg	27.6	16.0	34.1	2.2	189	.000
Mercury	Hg	mg/kg	0.2	0.1	0.3	.01	1.86	.000
Lead	Pb	mg/kg	43.9	26.0	52.2	3.8	364.0	.000
Nickel	Ni	mg/kg	13.3	10.0	10.4	1.5	67.0	.010
Selenium	Se	mg/kg	2.6	1.5	1.6	0.5	6.5	.000
Tin	Sn	mg/kg	3.0	1.4	5.9	0.3	54.0	.000
Zinc	Zn	mg/kg	252	131	348	14	2380	.000
Manganese	Mn	mg/kg	200	169	15	30	951	.045
Calcium	Ca	%	1.4	0.8	0.2	0.1	7.8	.001
Iron	Fe	%	1.4	1.1	0.1	0.2	7.7	.001
Magnesium	Mg	%	1.7	0.1	0.1	0.2	7.9	.017
Sodium	Na	%	0.4	0.4	0.03	0.1	1.8	.001
Potassium	K	%	0.8	0.8	0.03	0.2	1.8	.535
Phosphorus	P	mg/kg	1300	854	1615	113	11970	.000
Nitrogen	N	mg/kg	1290	957	1128	104	4910	.016

Stdv: standard deviation, min: minimum, max: maximum, K-S test: Kolomogorov-Smirnov test

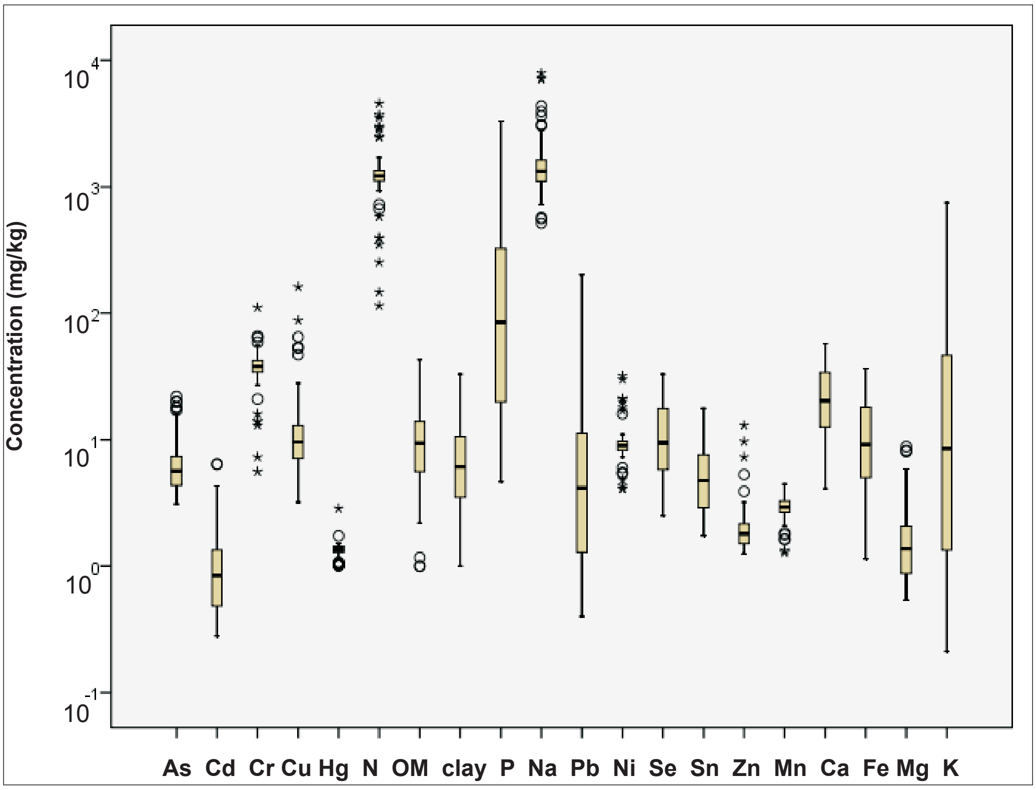

Figure 3. Boxplots for (log-transformed) major and trace element concentrations, organic matter (OM) and clay content of the sediments analyzed in this study (n = 105). • The median is indicated by a thick black line inside the box. A minor outlier (denoted by a "o") is an observation 1.5 x IQR (interquartile range) outside the central box. A major outlier (denoted by a "*") is an observation 3.0 x IQR outside the central box.

Data observations which lied more than 1.5 interquartile range lower than the first quartile or 1.5 interquartile range higher than the third quartile were considered as an outlier. In fact each variable was characterized by one or more outliers that were analyzed in more detail. Elevated heavy metal concentrations could generally be related to pollution sources in specific rivers. At two locations in the Nete catchment, elevated Fe-concentrations were found (7.49 and 7.66% Fe), which could be explained by the occurrence of iron-bearing sands and sandstone as well as glauconite in the subsoil. The occurrence of iron-bearing sands and sandstone and glauconite in the subsoil was derived from geological maps and from field observations during previous studies (e.g. Cappuyns and Swennen, 2007). At several locations, enhanced As-concentrations were measured in the river sediments together with the occurrence of high Fe-concentrations. A positive linear correlation between total Fe- and As-concentrations in soils and sediments has also been found by Huisman et al. (1997) in the southern part of The Netherlands, by Cappuyns et al. (2002) in the Demer catchment and by Horckmans et al (2004) in the Grand-Duchy of Luxemburg.

Another explanation for local enhanced Fe-concentrations in river sediments may relate to the formation of authigenic Fe-sediments. In the Nete basin (Flanders, Belgium) chemical precipitates derived from groundwater-associated Fe^{2+} seeping into the overlying surface water significantly contribute to the composition, concentration, and fluxes of suspended sediment (Van Lierde et al., 2007). Iron oxide surfaces are known to be very effective in adsorbing arsenic in soils and sediments (Waychunas et al., 1993).

Another type of authigenic minerals that may appear in sediments are Fe-sulfides, that can form porous aggregates that replace precursor oxides and hydroxides (Moles et al., 2003).

3.2 Variation in clay, organic matter and Fe content between river catchments

The results of the ANOVA test indicate that the organic matter contents did not significantly differ between river catchments (F-test = 1.365 with p = 0.209). For the clay content, however, a significant difference was found between river catchments (F-test = 2.379 with p = 0.014). The clay content of the river sediments was in the range 1 to 32%, with some extreme values (outliers) in the catchments of Lower Scheldt (30%), Ijzer (32%, 21 % and 22%), Brugse Polders (22%, 24% and 25%) and Leie (20%). Additionally, there is a clear increase in the clay content from east to west, with the lowest average values for the clay contact on the catchments of Meuse, Nete, Demer and Dijle-Zenne and highest average values in the catchments of Ijzer, Gentse Kanalen and Brugse Polders (Fig. 2). This increase is in accordance with the geological substrates that become more clayey. It has to be mentioned that only one sample of the catchment of the Upper Scheldt was analyzed in this study. However, several other studies (Vandecasteele et al., 2003; Cappuyns et al., 2004) also found a high clay content (average clay content 29% with values between 10 and 53%) of river sediments in this catchment.

The average total Fe-content of the sediments was not significantly different between the river catchments, but an important variation in Fe-concentrations was found within some river catchments. For example, in the Ijzer catchments, total Fe-concentrations were in the range of 0.49 to 4.20%, and elevated Fe-concentrations measured at some locations could be related to the occurrence of Fe-rich sands and sandstones in the subsoil.

3.3 Correlation matrix

Two-tailed Pearson correlations were determined based on the log-transformed values (Table 4). All variables were significantly ($p<0.001$) correlated with the clay and organic matter content, except K, Se, Zn, IR and pH. Se was only weakly correlated with other elements: only with Cd a correlation with a significance of 1% was found. The strong correlations between clay content (<2 μm fraction), some major elements (Mg, Na, K and Ca) and heavy metals (Cu, Cr, Hg, Ni and Pb) are explained by the association of these elements with clay-size minerals and other silicates (phyllosilicates, feldspars) that are also present in silt fractions.

Additionally, a significant positive linear correlation (0.01 significance level) was found between the total content of Fe and As ($R = 0.709$), Fe and Cr ($R = 0.654$) Š. and Fe and Cd, Cu, Hg and Ni (correlation coefficient around 0.5). A similar correlation between As and Fe-concentrations in surface soils in the Grand Duchy of Luxemburg was found by Horckmans et al. (2004). Baize and Sterckeman (2001) analyzed soil samples from Dornach (Switzerland), in which Cu, Co, Cr, Ni and Pb concentrations were also positively correlated with the Fe-content. In England and Wales, a similar correlation was found between heavy metals and Fe and Al (Zhao et al., 2007). As such, Fe may be an important variable to take into account when background values of heavy metals are deduced from physico-chemical soil and sediment properties.

3.4 Factor analysis

Both the Kaiser-Meyer-Olkin test (0.893) and the Barlett's test (chi^2 = 2125.95 with $p < 0.001$) indicate that the Š. dataset was appropriate to perform a factor analysis (FA). The result of the FA analysis for heavy metals, major elements, organic matter and clay content are presented in Table 5. Oxygen content, dry matter content and temperature of the river water were not included in the FA, since emphasis was placed on physico-chemical sediment properties related to lithology. Based on the FA analysis, 4 components were extracted, with an eigenvalue > 1 before and after rotation. The first component explained 34% of the total variance in the dataset and was representative for a component including clay (< 2 μm fraction), organic matter, Na, Ca, Mg, K and Mn but also some trace elements such as Ni, Cu, Cr, Pb, Hg. Calcium, Mg, K and Na are, besides Al, Si and O, important constituents of phyllosilicates and feldspars. Concentrations of heavy metals are often related to the clay (< 2 μm fraction) and organic matter content in soils

Table 4. Pearson Correlation matrix. Correlation coefficients with p<0.001 are indicated in bold (DM = Dry matter, OM = Organic matter)

	As	Ca	Cd	clay	Cr	Cu	DM	Fe	Hg	IR	K	Mg	Mn	N	Na	Ni	OM	P	pH	Pb	Se	Sn	Zn
As	##	**,466**	**,611**	**,617**	**,645**	**,590**	**-,468**	**,696**	**,585**	-,154	-,114	**,596**	**,589**	**,599**	**,338**	**,657**	**,686**	**,659**	-,219	**,517**	,194	**,428**	**,518**
Ca		##	,274	**,591**	**,602**	**,619**	**-,506**	**,417**	**,620**	**-,376**	-,157	**,903**	**,662**	**,580**	**,737**	**,612**	**,648**	**,413**	-,308	**,617**	,125	**,419**	**,434**
Cd			##	**,349**	**,505**	**,509**	**-,379**	**,560**	**,535**	-,125	-,196	**,375**	**,503**	**,422**	,100	**,583**	**,426**	**,536**	-,211	**,517**	,135	**,411**	**,475**
clay				##	**,713**	**,670**	**-,684**	**,601**	**,592**	-,210	-,114	**,724**	**,642**	**,781**	**,665**	**,757**	**,764**	**,543**	-,276	**,623**	,217	**,401**	**,471**
Cr					##	**,714**	**-,573**	**,637**	**,710**	-,211	-,133	**,723**	**,595**	**,647**	**,517**	**,818**	**,625**	**,642**	**-,325**	**,648**	,212	**,397**	**,608**
Cu						##	**-,614**	**,497**	**,769**	-,107	-,008	**,623**	**,617**	**,757**	**,556**	**,819**	**,662**	**,633**	-,284	**,799**	,293	**,591**	**,644**
DM							##	**-,544**	**-,535**	,159	,231	**-,565**	**-,521**	**-,833**	**-,500**	**-,635**	**-,677**	**-,461**	,258	**-,544**	-,001	**-,385**	**-,420**
Fe								##	**,462**	-,130	-,036	**,649**	**,617**	**,600**	**,267**	**,576**	**,653**	**,697**	-,128	**,416**	,164	**,379**	**,427**
Hg									##	-,282	-,125	**,659**	**,531**	**,569**	**,444**	**,713**	**,631**	**,506**	**-,367**	**,708**	,143	**,491**	**,543**
IR										##	,170	**-,364**	-,129	-,113	**-,366**	-,118	-,270	,041	,255	-,214	,007	-,105	-,113
K											##	-,158	-,084	-,110	-,080	-,185	-,162	,027	**,448**	-,127	,104	,003	-,108
Mg												##	,710	**,631**	**,699**	**,687**	**,724**	**,502**	-,340	**,593**	,151	**,375**	**,451**
Mn													##	**,578**	**,452**	**,719**	**,615**	**,640**	-,197	**,647**	,197	**,417**	**,432**
N														##	**,596**	**,738**	**,779**	**,649**	-,250	**,644**	,134	**,519**	**,473**
Na															##	**,525**	**,536**	**,274**	**-,341**	**,454**	,156	**,354**	**,353**
Ni																##	**,646**	**,621**	**-,348**	**,796**	,203	**,539**	**,609**
OM																	##	**,614**	-,288	**,600**	,170	**,351**	**,451**
P																		##	-,196	**,499**	,265	**,457**	**,479**
pH																			##	-,288	,080	-,184	-,233
Pb																				##	,188	**,607**	**,555**
Se																					##	,108	,195
Sn																						##	**,659**
Zn																							##

Table 5. Total variance explained and component matrix for the elements analyzed

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
1	11.69	53.15	53.15	11.69	53.15	53.15	7.58	34.44	34.44
2	2.0 4	9.26	62.42	2.03	9.26	62.42	4.00	18.19	52.63
3	1.40	6.38	68.80	1.40	6.38	68.80	3.01	13.67	66.29
4	1.07	4.85	73.65	1.07	4.85	73.65	1.62	7.35	73.65
5	.94	4.27	77.92						
6	.70	3.16	81.08						
7	.68	3.09	84.16						
8	.49	2.22	86.39						
9	.43	1.95	88.33						

Element	Component matrix				Rotated component matrix			
Component	1	2	3	4	1	2	3	4
As	.764		.230	-.300	.406	.748		
Cd	.602	.428		-.411		.722	.430	
Cr	.848				.629	.473	.319	
DM	-.741			-.222	-.724	-.241		
P	.735	.386	.221		.399	.643	.321	.260
OM	.838				.710	.466		
Cu	.854			.242	.698	.264	.508	
clay	.844		.200		.827	.337		
Hg	.792		-.266		.535	.346	.503	-.210
Pb	.798		-.307		.584	.229	.611	
Ni	.887				.680	.398	.443	
Se		.441	.367					.579
N	.845			.241	.796	.307	.224	
Sn	.402	.389	-.627				.812	
Zn	.488	.538	-.389	.219	.200		.793	.213
I.R.	-.273	.516	.384	.466				.812
Ca	.772	-.385			.753			-.370
Fe	.729		.391	-.369	.396	.822		
Mg	.854	-.334			.753	.409		-.327
Mn	.789				.573	.497	.246	
Na	.655	-.544		.282	.856			-.269
K	.804	-.310			.710	.431		-.273
pH	-0.386	0.537	.405	.172	-.085	-.273	-.292	.670

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Only the first four components are represented

and sediments. Moreover, quartz can be considered as a diluting phase for trace elements, resulting in lower trace element concentrations when the quartz content (that is mainly found in the coarser grainsize fractions) increases. The second component accounted for 18% of the total variance in the dataset and indicated a relationship between Fe, As and Cd, although several other elements such P and N are also associated with the second axis, which likely indicates elements with an antropogenic origin (e.g. N, P from agricultural origin). The third component, which was determined by Cd, Cu, Hg, Pb, Ni, Sn and Zn could be considered as a metal group, which also has a major anthropogenic origin, but from a different source and/or with a different geochemical behavior in comparison to elements from the second axis. The fourth component was mainly determined by the insoluble residue and pH, but the relationship between between both variables is not clear. The insoluble residue mainly consists of non-dissolved quartz particles (observed under the binocular). The more sandy and more quartz-rich soils of the northern part of Belgium (Nete and Meuse catchment) are characterized by a slightly lower pH compared to the more clayey soils in the western part of Belgium and the loess-derived soils in central Belgium, but for river sediments this relationship between pH and quartz content has not been established so far. Most of the variables were explained rather well by the four components (communalities > 0.7), except Se.

3.5 Multiple linear regression

Multiple linear regressions were performed with Fe, Ca, I.R., pH, clay (< 2μm fraction) and organic matter (OM) as independent variables. Clay and organic matter were included because they are already used in the standardization of background values for heavy metals in soils and sediments (ŒVLAREBO, 2066). Fe is a major component of Fe(hydr)oxides, but is also a constituent of clay minerals. In soils and sediments, Ca is dominantly found in clay minerals and in carbonate minerals (e.g. $CaCO_3$). Finally, the insoluble residue and pH were also included because they constituted one of the components that explained the variance in the dataset. However, the link between the insoluble residue and the pH is not clear.

Table 6. Regression equations of the log-transformed parameters (a) for the complete dataset (b) after omission of outliers (based on the boxplot). OM = organic matter

Element	Regression equation	R^2-
Log (As)	^{a}= 0.512 + 0.441 log (Fe) + 0.375 log (OM)	0.760
	^{b}= 0.482 + 0.396 log (OM) + 0.384 log (Fe)	0.775
Log (Cd)	^{a}= - 0.111 + 0.656 log (Fe)	0.560
	^{b}= -0.370 + 0.354 log (Fe) + 0.188 log (OM)	0.627
Log (Cr)	^{a}= 1.101 + 0.390 log (clay) + 0.342 log (Fe) + 0.188 log (Ca)	0.785
	^{b}= 1.129 + 0.317 log (clay) + 0.375 log (Fe) + 0.193 log (Ca)	0.809
Log (Cu)	^{a}= 0.524 + 0.425 log (clay) + 0.320 log (Ca) + 0.331 log (OM) + 0.189 log (I.R.)	0.751
	^{b}= 0.667 + 0.270 log (OM) + 0.288 log (Ca) + 0.334 log (clay)	0.739
Log (Hg)	^{a}= -1.549 + 0.577 log (OM) + 0.387 log (Ca)	0.689
	^{b}= -1.454 + 0.392 log (Ca) + 0.394 log (OM)	0.676
Log (Pb)	^{a}= 1.107 + 0.475 log (clay) + 0.338 log (Ca)	0.696
	^{b}= 1.135 + 0.319 log (Ca) + 0.367 log (clay)	0.681
Log (Mn)	^{a}= 2.063 + 0.270 log (Ca) + 0.325 log (Fe) + 0.190 log (clay)	0.775
	^{b}= 2.012 + 0.295 log (Ca) + 0.311 log (Fe) + 0.181 log (clay) + 0.126 log (I.R.)	0.787
Log (Ni)	^{a}= 0.696 + 0.432 log (clay) + 0.147 log (Ca) + 0.155 log (Fe)	0.795
	^{b}= 0.696 + 0.421 log (clay) + 0.138 log (Ca) + 0.151 log (Fe)	0.794
Log (Se)	^{a}= 0.312 + 0.231 log (clay)	0.207
Log (Sn)	^{a}= 0.286 + 0.254 log (Ca)	0.271
	^{b}= -0.095 + 0.329 log (OM)	0.248
Log (Zn)	^{a}= 1.811 + 0.409 log (OM)	0.346
	^{b}= 1.822 + 0.310 log (OM)	0.319

Regression equations were constructed according to the stepwise method (Carlon et al., 2003) in order to only include the most significant independent variables. Most heavy metal concentrations could be predicted very well by the independent variables, except Zn, Se and Sn (Table 6). An example of a good fit between measured and predicted values is presented in Fig. 4 for Cr. Cd- and As-concentrations could be predicted with Fe and organic matter as independent variables.

For the other trace elements, Ca, clay, Fe and/or organic matter were included in the regression equations, allowing to explain more than 60% of the variation of heavy metal concentrations in the sediments. These results are in line with results of Zhao et al. (2007), who could explain 62 to 85% of the variance of heavy metal concentrations in soils by using Fe and Al as independent variables in their regression equations. The removal of outliers from the dataset did not significantly improve the regression equations.

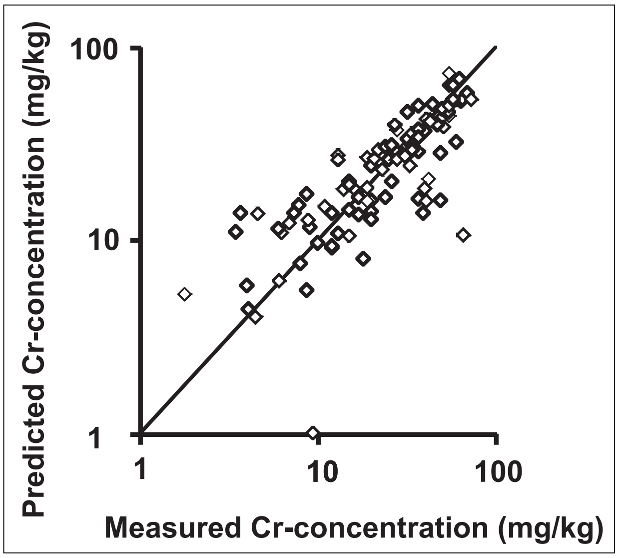

Figure 4. Measured versus predicted Cr-concentrations in the sediments (in mg/kg; log-scale).

Despite the fact that major elements such as Ca and Fe are also a component of clay minerals, they are also major components of resp. Fe-(hydr)oxides and carbonates. Moreover, the attribution of the term ‘clay fraction’ to the < 2μm fraction is sometimes misleading. Besides clay-minerals, Fe-rich accessory minerals such as Fe-oxi/hydroxides and phylosilicates are often concentrated in the clay fraction (< 2μm) (Schulze, 1988). A geochemical approach using the total concentrations of conservative elements may be used to overcome these difficulties (e.g. Covelli & Fontolan, 1997). Before processing the dataset, the potential anthropogenic input of the element and diagenetic processes that may alter its concentrations in sediments should be checked (Schiff & Weisberg, 1999). For example, at some locations (e.g. in the Nete catchment), elevated Fe-concentrations in the sediments could be related to diagenetic processes resulting in the formation of authigenic Fe.

A few samples were characterized by extremely high Ca-concentrations (between 7.08 and 7.82 %) and a high pH (8.5-8.6). In these outliers, the presence of an important amount of Ca and the alkaline pH was explained by the presence of a wastewater treatment plant nearby the sampling points and not related to the presence of carbonated sediments.

In further investigations, the applicability of the obtained regression equations should be tested in other applications, and the inclusion of Fe and Ca in regression equations that are applied for the standardization of total metal concentrations in soils and sediments, should be considered.

4. Conclusion

When the composition of soils and sediments is investigated, attention is mainly paid to the concentrations of heavy metals, concentrations of organic contaminants, pH, organic matter and clay content. The results from this study, performed on a dataset of 105 riverbed sediments originating from Flanders, indicate that, besides organic matter and clay content, other variables such as the total Fe and Ca content can be relevant parameters to predict heavy metal concentrations. Indeed after multiple linear regression analysis, equations were obtained that, also included total concentrations of Fe and Ca.

5. Acknowledgements

Grateful acknowledgements are made to Gilles Colinet for his helpful suggestions to improve the manuscript.

6. References

BAIZE, D. & STERCKEMAN, T., 2001. Of the necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. *Science of the Total Environment*, 264: 127-139.

BÖLVIKEN, B., BOGEN, J., DEMETRIADES, A., DE VOS, W., EBBING, J., HINDEL, R., LANGEDAL M., LOCUTURA J., O’ CONNOR P., OTTESEN R.T., PULKKINEN E., SALMINEN R., SCHERMANN O., SWENNEN R., VAN DER SLUYS J. & VOLDEN T., 1996. Regional geochemical mapping of Western Europe towards the year 2000. *Journal of Geochemical Exploration,* 56: 141-166.

CAPPUYNS, V., SWENNEN, R. & DE NIL, K. 2002. Heavy metals and arsenic in alluvial sediments of the Grote Beek river (N Belgium): contribution of natural and antropogenic sources. *Aardkuindige Mededelingen,* 12: 227-230

CAPPUYNS, V., SWENNEN, R. & DEVIVIER, A., 2004. Influence of ripening on pHstat leaching of heavy metals from dredged sediments. *Journal of Environmental Monitoring,* 6(9): 774-781.

CAPPUYNS, V. & SWENNEN, R. 2007. Classification of alluvial soils according to their potential environmental risk: a case study for Belgian catchments. *Journal of Environmental Monitoring,* 9, 319-328.

CARLON, C., DALLA VALLE, M. & MARCOMINI, A., 2003. Regression models to predict water-soil heavy metals partition coefficients in risk assessment studies. *Environmental Pollution*, 127 (1), 109-115.

CHAPMAN, P.M., 1990. The sediment quality triad approach to determining pollution-induced degradation. *Science of the Total Environment,* 97-98: 815–825.

CROMPTON T.R., 2000. *Determination of organic compounds in soils, sediments and sludges Taylor and Francis*, 1st edition, p. 298.

COVELLI, S. & FONTOLAN, G., 1997. Application of a normalization procedure in determining geochemical baselines, Gulf of Trieste, Italy. *Environmental Geology* 30(1-2), 34-45.

DE COOMAN, W. & DETEMMERMAN L., 2003. Waterbodemonderzoek in Vlaanderen : Hoe gaan we te werk en wat zijn de eerste meetresultaten? (Sediment Quality Assessment in Flanders: how do we go about it and what are measuring results?) *Water,* 6, 1-7.

DE TEMMERMAN, L., VANONGEVAL, L., BOON, W., HOENIG, M., & GEYPENS, M., 2003. Heavy metal content of arable soils in Northern Belgium. *Water,- Air,- and Soil Pollution*, 148, 61-76.

DIEZ, M., SIMON, M., DORRONSORO, C., GARCIA, I., & MARTIN, F., 2007. Background arsenic concentrations in Southeastern Spanisch soils. *Science of the Total Environment*, 378 (1-2), 5-12.

FLEMISCH ENVIRONMENTAL AGENCY 2009. Flemisch sediment monitoring network. http://www.vmm.be/water/toestand-watersystemen/waar-meten-we-het-water/meetnet_waterbodems.html

HORCKMANS, L., SWENNEN, R., DECKERS. J., & MAQUIL. R., 2004. Local background concentrations of trace elements in soils: a case study in the Grand Duchy of Luxembourg. *Catena*, 59 (3), 279-304.

HUISMAN, D.J., VERMEULEN, F.J.H., BAKER, J., VELDKAMP, A., KROONENBERG, S.B., KLAVER, TH., 1997. A geological interpretation of heavy metal concentrations in soils and sediments in the southern Netherlands. *Journal of Geochemical Exploration*, 59(3): 163-174.

ISO standard 11277:1998. Soil quality -- Determination of particle size distribution in mineral soil material -- Method by sieving and sedimentation, International Organization for Standardization, 30pp.

ISO standard 11466:1995 Soil quality -- Extraction of trace elements soluble in aqua regia, International Organization for Standardization, 6pp.

LELOUP, V., DE COOMAN, W., MEIRE, P. & DE DECKERE E., 2007. Ontwikkeling van ecologische en ecotoxicologisch onderbouwde kwaliteitsdoelstellingen voor waterbodems (Development of ecological and ecotoxicological quality criteria for riverbed sediments). *Water*, 26: 88-91

MARQUES, J.J., SCHULZE, D.G., NILTON CURI, N., STANLEY, A. & MERTZMAN, S.A., 2004. Major element geochemistry and geomorphic relationships in Brazilian Cerrado soils. *Geoderma*, 119(3-4): 179-195.

MARTÍNEZ CORTIZAS, A., GARCÍA-RODEJA GANOSO, E., NÓVOA MUÑOZ, J.C., X. PONTEVEDRA POMBAL, X., BUURMAN, P. & TERRIBILE F., 2003. Distribution of some selected major and trace elements in four Italian soils developed from the deposits of the Gauro and Vico volcanoes. *Geoderma*, 117 (3-4): 215-224.

MICÓ, C, RECATALÁ, L., PERIS, M., & SÁNCHEZ, J., (2006). Assessing heavy metal sources in agriculural soils of an European Mediterranean area by multivariate analysis. *Chemosphere*, 65 (5): 863-872.

MOLES, N.R., BETZ, S.M., MCCREADY, A.J., MURPHY, P.J., 2003. Replacement and authigenic mineralogy of metal contaminants in stream and estuarine sediments at Newtownards, Northern Ireland. *Mineralogical Magazine,* 67 (2): 305-324.

NEFF, J.C., REYNOLDS, R, SANFORS Jr., R. L, FERNANDEZ, D. & LAMOTHE P., 2006. Controls of Bedrock Geochemistry on Soil and Plant Nutrients in Southeastern Utah. *Ecosystems*, 9(6): 879-893.

OTTESEN, R.T., BOGEN, J., BØLVIKEN, B., VOLDEN, T.,1989. Overbank sediment: a representative sample medium for regional geochemical mapping. *Journal of Geochemical Exploration,* 32: 257-277.

ROCA, N., SUSANA PAZOS, M. & BECH, J., 2008. The relationship between WRB soil units and heavy metals content in soils of Catamarco (Argentina). *Journal of Geochemical Exploration,* 96 (2-3): 77-85.

SALONEN, V.-P. & KORKKA-NIEMI, K., 2007. Influence of parent sediments on the concentration of heavy metals in urban and suburban soils in Turku, Finland. *Applied Geochemistry,* 22 (5*):* 906-918.

SALVADOR-BLANES, S., CORNU, S. & KING, D., 2002. Distribution d'un élément trace (Cr) dans un sol développé sur roches métamorphiques : variabilité à l'échelle d'un versant-Distribution of chromium in soils developed into metamorphic rocks: variability at the hillslope scale. *Comptes Rendus Geosciences*, 334(1): 51-58

SCHIFF, K. & WEISBERG, S. B., 1999. Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. *Marine Environmental Research*, 38 (2): 161-176.

SCHULZE, D.G., 1988. Separation and concentration of iron-containing phases. *In* J.W. Stucki, B.A. Goodman & U. Schwertmann (eds). *Iron in soils and clay minerals.* Reidel Publishing Companies, Dordrecht, Boston, Lancaster & Tokio, pp. 63-81.

SONDAG, F. & DUCHESNE, J.C., 1987. The use of geiochemical methods to characterize the methamorphic domain in the Belgian Ardennes. *Journal of Geochemical Exploration,* 27: 311-321.

STERCKEMAN, T., DOUAY, F., BAIZE D., FOURRIER, H., PROIX, N. & SCHVARTZ C., 2006. Trace elements in soils developed in sedimentary materials from Northern France. *Geoderma,* 136(3-4): 912-929.

SUMMERS, J.K., WADE, T.L., ENGLE, V.D. & MALAEB, Z.A., 1996. Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries* 19(3), 581-594.

SWENNEN, R., VAN DER SLUYS, J. & HINDEL, R., 1996. Geochemical characterisation of overbank sediments: a way to assess background reference data and environmental pollution in highly industrialised areas (such as Belgium and Luxembourg). *Zentralblatt für Geologie und Paläontologie,* 1 : 925-942.

SWENNEN, R. & VAN DER SLUYS, J., 1998. Zn, Pb, Cu and As distribution patterns in overbank and medium-order stream sediment samples: their use in exploration and environmental geochemistry. *Journal of Geochemical Exploration,* 65: 27-45.

SWENNEN, R., VAN DER SLUYS, J., HINDEL, R. & BRUSSELMANS, A., 1998. Geochemistry of overbank and high-order stream sediments in Belgium and Luxembourg: a way to assess environmental pollution. *Journal of Geochemical Exploration,* 62: 67-79.

SWENNEN, R. & VAN DER SLUYS, J., 2002. Anthropogenic impact on sediment composition and geochemistry in vertical overbank profiles of river alluvium from Belgium and Luxembourg. *Journal of Geochemical Exploration*, 75 (1-3): 93-105.

TACK, F.M.G., VERLOO, M.G., VANMECHELEN, L., & VAN RANST, E., 1997. Baseline concentrations levels of trace elements as a function of clay and organic carbon contents in soils in Flanders (Belgium). *Science of the Total Environment*, 201 (2): 113-123.

VANDECASTEELE, B., DE VOS, B. & TACK, F.M.G., 2003. Temporal-spatial trends in heavy metal contents in sediment-derived soils along the Sea Scheldt river (Belgium). *Environmental Pollution*, 122(1): 7-18.

VANLIERDE, E. DE SCHUTTER, J., JACOBS, P. & MOSTAERT, F., 2007. Estimating and modeling the annual contribution of authigenic sediment tot the Total suspended sediment load in the Kleine Nete Basin, Belgium. *Sedimentary Geology*, 202, 317-332.

VLAREBO, 2006. Vlaams reglement betreffende de bodemsanering. Decree on Soil Remediation and Soil protection; ratified by the Flemish Government. on 27 October 2006.

WAYCHUNAS, G.A., REA, B.A., FULLER, C.C. & DAVIS, J.A., 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochimica Cosmochimica Acta,* 57: 2251–2269

WEBSTER, R., 1997. Regression and functional relations. *European Journal of Soil Science*, 48: 557-566.

WEBSTER, R., 2001. Statistics to support soil research and their presentation. *European Journal of Soil Science*, 52: 331-340.

ZHAO, F.J., MCGRATH, S.P., & MERRINGTON, G., 2007. Estimates of ambient background concentrations of trace metals in soils for risk assessment. *Environmental Pollution*, 148 (1): 221-229.

Manuscript received 27.11.209, accepted in revised form 19.03.2010, available on line 15.05.2010.