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Background values of cobalt in Flemish and European soils

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ABSTRACT. Despite the fact that some European countries established threshold values for cobalt (Co) in soil, no limit values for Co are defined in Flanders (Belgium). Moreover, relatively few data are available concerning the Co content of uncontaminated soils. In the present work, the occurrence of Cobalt in soil was assessed based on the analysis of two databases: The first dataset consisted of 80 non-contaminated soil samples from Flanders, selected out of a dataset of 2300 soil samples taken within the framework of soil investigations in the period 1995-2009. Secondly, the database of the European FOREGS project was used, including the analytical results of 837 topsoil samples and 784 subsoil samples. The Co content of the soil samples was in the range 0.27–255 mg/kg dry matter and background values in the range 11-14 mg/kg were calculated. Moreover, regression equations with major elements, clay and organic matter content as independent variables were established in order to predict the Co content in European soils (FOREGS dataset). Both in topsoil and subsoil samples, Fe_2O_3 and MnO were independent variables that most significantly explained the total content of Co in soil.

KEYWORDS: background value, contamination, multiple regression, soil, trace metals

1. Introduction

1.1. Occurrence, sources and applications of Cobalt

Cobalt is a transition element with a density of 8.9 g/cm^3 and according to Bjerrum's (1936) definition of heavy metals it can be classified as a heavy metal, with a density above 7 g/cm^3. Nieboer & Richardson (1980) developed an alternative classification scheme in which metal ions were placed in two classes: Class A ions preferably form ionic bounds and are easily displaced and mobile, while Class B ions form covalent bounds and show strong affinity to soft ligands such as sulphide or sulphur donors. Moreover, class B metal ions tend to accumulate in organisms with resultant toxicity. In this classification system, Co is considered a 'Class B metal' or borderline metal.

Cobalt is a natural component of the Earth's crust, with an average concentration of 25 mg/kg. In basalt, Co concentrations are in the range 40-50 mg/kg, while much lower concentrations, between 1 and 10 mg/kg are found in granite (Barceloux, 1999).

In nature, Co is usually not found as pure metallic element, but mainly as sulphides, oxides and arsenides, with Co_3S_4, $CuCo_2S_4$, $CoAs_2$, $CoAs_3$, $Co_3(AsO_4)_2.8H_2O$ and CoAsS being the most common Co minerals (ATSDR, 2004). Significant amounts of Co are also stored in the deep seas. The total amount of Co in the Pacific Ocean is estimated to be in the range 2.5 to 10 million tons. The principal ore bodies that contain Co in high concentrations are the Cu-Co deposits of the Katanga type, Ni-Co deposits of the Sudbury type, arsenide vein deposits of the Bou-Azzer type and Ni laterite ores formed by the weathering and leaching of some types of rock under tropical conditions (Hamilton, 1994).

Since cobalt naturally occurs in nickel bearing laterites and nickel-copper sulphide deposits it is most often extracted as a by-product of nickel and copper. According to the Cobalt Development Institute (Kapusta, 2007), about 48% of cobalt production originates from nickel ores, 37% from copper ores and 15% from primary cobalt production.

Cobalt is used in the preparation of magnetic, wear-resistant and high-strength alloys. One of the most known applications of Co is its use as a negative electrode in rechargeable Ni/Co batteries. Since 1980, one third of the total amount of Co that is produced, is used in the chemical industry, mainly as catalyst of chemical reactions in the petrochemical and plastic industry.

As consequence of weathering and transport processes, Co also occurs in soil, groundwater and surface waters. Co exists in two oxidation states, Co(II) and Co(III) (Kabata-Pendias & Pendias, 2001, Beak et al., 2011). In the absence of organic ligands, Co exhibits a high affinity for mineral surfaces, especially Mn- and Fe(hydr)oxides. (McLaren et al., 1986; Barrow & Whelan, 1998, Beak et al., 2011). A study of Wendling et al. (2009) indicated that the potential biological availability of Co generally declines with time across a broad range of soils. Excessive levels of Co are considered poisonous and can cause significant health problems, but Co is also an essential trace element for human and animal health. Co deficiency may affect livestock, resulting in impaired growth and other non-specific signs such as anorexia and anaemia (Reid & Horvath, 1980). In human beings, Co is an important element in the formation of cobalamin or vitamin B12 and it is required for the normal functioning of the pancreas.

1.2. Environmental legislation and soil

The definition of 'soil' from a scientific point of view slightly differs from the definition in environmental legislation. Since this study has a scientific purpose, but also wants to formulate some advice towards environmental policy makers, the use of the term 'soil' will first be clarified.

In scientific terms, "soil" can be defined as a "three-dimensional body with properties that reflect the impact of climate, vegetation, fauna, and topography on soils parent material over a variable time span". Soils are still in a process of change. As a result of 'soil formation' or 'pedogenesis', soil profiles show signs of differentiation or alteration of the 'soil material' (Driessen & Dudal, 1991). In the Flemish legislation on soil contamination and soil protection, soil is defined as "the solid phase of the earth, including groundwater, and all other occurring components or organisms". This implies that, from a legal point of view, groundwater is also considered a part of the soil. In the present study, however, only the solid phase of the soil, without groundwater, porewater and living organisms will be considered.

For a number of heavy metals (Cd, Cu, Cr, Hg, Ni, Pb and Zn), arsenic and organic contaminants, threshold concentrations have been determined in the Flemish Soil Legislation, including background values, target values and remediation values. These values are defined as a function of organic matter content, clay content (< 2µm fraction) and pH(KCl) of the soil. In Belgium, Co is not taken into account when the environmental quality of soils has to be evaluated, despite the existence of several (diffuse) sources for Co, such as non-ferrous metal smelters and coal combustion (VMM, 2013).

In the environmental legislation of Flanders and Wallonia (which are the two main regions in Belgium, each with an own environmental legislation), threshold cobalt concentrations are only defined for emissions in air, surface water and groundwater. Nevertheless, several European countries established norm values for Co in soils (Table 1). The norm values in Table 1 differ because of the use of different models, software and criteria with regard to human toxicology and ecotoxicology (Provoost et al., 2006). Additionally, natural (background) concentrations of trace elements in soils and sediments are dependent on soil and sediment properties (clay content, organic carbon content,…) and

Country	Negligible risk	Alarming risk	Unacceptable risk (residential area)	Unacceptable risk (industry)
Finland		20	100	250
Italy			20	250
Lithuania			30	
The Netherlands	0.38		240	
Poland			45	175
Slovakia	20	50	300	
Czech Republic	25	180	300	
Sweden		200		

Table 1. Norm values for cobalt (total concentration in mg/kg) in soil in European countries (Provoost et al., 2006; Carlon, 2007)

on the geological substratum, which makes it difficult to compare these norm values (Spurgeon et al., 2008).

The aim of this study was to (1) evaluate the Co content of soils in Flanders and Europe and to compare these values with norm values established in other European countries (2) to establish regression equations that allow to explain the Co content in soils based on major element composition and/or physico-chemical soil properties such as clay and organic matter content

1.3. Background concentrations of Co in soil

It is not the purpose of the present study to give a review of all possible methods to determine background concentrations of elements in soil. A comprehensive overview is given in Dung et al. (2013) and some of the methods discussed in this paper will be applied here.

Background values of trace elements in soil can be defined as 'natural' concentrations of these elements in a soil that are not influenced by anthropogenic contamination (Salminen & Gregorauskiene, 2000; Adriano, 2001). In Western Europe, and certainly in Flanders, it is very difficult to find virgin soils that have not been subjected to any anthropogenic influence, because of the high population density, the important industrial activities and because of atmospheric deposition of contaminants far away from pollution sources. As a consequence, the determination of background values of trace elements based on the composition of virgin or pristine soil samples is rather difficult. In literature, several methods are proposed to calculate representative background values for trace elements in soils. Micó et al. (2007) used a statistical approach to calculate background values of different trace elements in Spanish soils. The formula (X + 2 S) was used to calculate the background values, with X the average concentration of a trace element and S the standard deviation. This approach has also been followed by Tack et al. (1997) and Gil et al. (2004) to deduce background values of trace elements in Flemish and Spanish soils respectively. Another method that is sometimes applied to calculate background values, consists of 95th percentile value of a trace element in a dataset, which has for example been applied by Brus et al. (2009) to determine background concentrations of trace elements in Dutch soils.

The target values for soil quality, stated in Article 3 of the Order of the Flemish Government establishing the Flemish Regulations concerning soil remediation and protection, are based on 90th percentile values (De Temmerman et al., 2003). In order to take the soil characteristics into account while comparing the concentrations of heavy metals and metalloids in the unsubmerged land with the target values for the soil quality, the target values are converted, except for cadmium and mercury, to the measured levels of clay and organic material in the sample to be examined.

In Table 2, background values for Co in soil, determined in different European countries and by using different approaches, are presented.

2. Methodology

2.1. Sampling locations and sampling

2.1.1. Flemish samples

Sampling locations were selected from the soil database of the Flemish waste agency (OVAM) taking into account different criteria. The soil database of the Flemish waste agency contains analytical results of all soil investigations performed in Flanders, starting from October 1995. Within the framework of this paper, a selection of relevant soil samples was made based on well-defined criteria. Since Co is a not-regulated parameter and Co is thus not systematically determined within the framework of soil investigations, first the samples were selected for which Co was analyzed. In September 2010, the OVAM soil database contained the Co concentrations of 2324 soil samples. From the 2324 soil samples for which data on Co concentrations were available, the samples for which also the clay content, organic carbon content, Al and Fe were measured, were selected. An additional criterion was the variability of soil characteristics, in order to have a set of samples that is representative for the variation of soil characteristics found in Flanders. Therefore, the descriptions of soil profiles in the database of OVAM was consulted.

In a last selection step, only the sampling locations in areas where human influences are assumed to be minimal, were retained. Finally, 40 locations remained, distributed throughout the entire area of Flanders (Fig. 1) and located far away from metal processing industries, non-ferro industries, agricultural soils (possibly contaminated by the application of manure or sewage sludge) and highways. The geological substrate in Flanders is dominated by non-lithified Quaternary and Tertiary

Soil type	Co concentration (mg/kg)	Reference
Sandy soil (Flanders)	0.3 – 10	De Temmerman et al. (2003)
Loamsoil (Flanders)	5 – 15	De Temmerman et al. (2003)
Topsoil (Flanders)	0.03 – 7.7	Tack et al. (1997)
Topsoil (Spain)	11[a]	Mico et al. (2007)
Topsoil (The Netherlands)	15[b]	Brus et al. (2009)
Sandy and loamy sand soil (Lithuania)	4.3[c]	Carlon et al. (2007)
Loam and clay soil (Lithania)	6.4[c]	Carlon et al. (2007)
Sandy soil and podzol (Poland, Romania, US)	2 – 14	Kabata-Pendias (2001)
Loam and clay soil (Germany)	3 – 6	Schuiling (2003)
Forest soil (Russia)	0.6 – 45	Schuiling (2003)
Podzol and Sandy soil (Germany)	0.8 – 6	Schuiling (2003)
Soil on Bituminous shale (Luxembourg)	8 - 37	Horckmans et al. (2005)
Soil on Minette (Luxembourg)	12 - 95	Horckmans et al. (2005)

[a]determined via (X + 2 S), [b]determined via 95th –percentile value, [c]method not mentioned

Table 2. Background values for Co in soil found in scientific literature

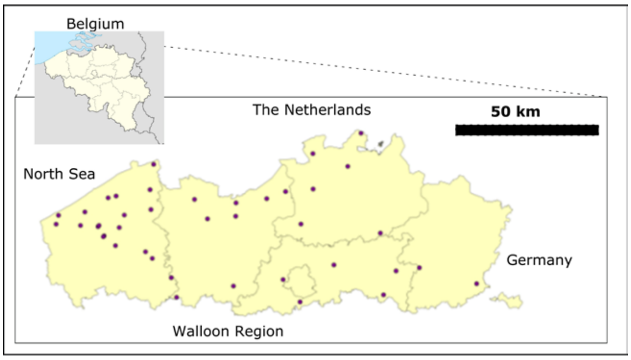

Figure 1. Overview of the 40 Flemish sampling locations

Sands. Because the relatively uniform geological substrate in this area, the dataset was not subdivided according to differences in lithology. However, differences in lithology are also reflected in the major element composition of the soil samples and thus indirectly taken into account.

At each sampling location, a topsoil sample (sampled between 0 and 50 cm depth) and a subsoil sample, (sampled between 50 and 100 cm depth) were taken, yielding 80 samples in total. For each sample, 1 kg was collected according to the recommendations described in the code of good practice for soil and groundwater sampling (OVAM, 2001). The collection of samples at two depths has the advantage that, despite the abovementioned selection of 'uncontaminated' samples, the effect of airborne depositions or other anthropogenic inputs can be detected by comparing subsoil and topsoil samples. For each sampling location, Lambert X-Y coordinates were available, which will only be used to present the sampling locations graphically, but will not be reported for reasons of confidentiality.

2.1.2. *European samples from the FOREGS Geochemical Baseline Mapping Programme*

"The FOREGS (FORum of European Geological Surveys) Geochemical Baseline Mapping Programme's main aim is to provide high quality, multi-purpose environmental geochemical baseline data for Europe. The need for this type of data was justified by the first Working Group on Regional Geochemical Mapping immediately after the Chernobyl accident in 1986, when it was realized that a baseline for radioactive and other polluting elements could not be defined (Bølviken et al., 1993, 2000)." (Salminen et al., 2005). After several attempts to compile existing regional geochemical databases in Europe, it was clear that the establishment of a harmonized European wide geochemical database was essential. The FOREGS Directors approved a Geochemical Baseline Mapping Programme in 1996 and in 1997 an agreement on the principles of field and analytical methodologies was obtained and the field methodology was tested, finally resulting in the "FOREGS Geochemical Field Manual", that was published in 1998 (Salminen et al., 1998). In the present study, data from topsoil and subsoil samples in 26 countries that were involved in the FOREGS Geochemical Baseline Mapping Programme are used.

Each soil sample was a composite of 3 to 5 sub samples collected from pits located at a distance of 10-20 meters from each other. Living surface vegetation, fresh litter, large roots and rock fragments (stones) were first removed by hand. The topsoil sample was taken at a depth of 0-25 cm (excluding material from the organic layer where present), and a subsoil sample was taken from a 25 cm thick section within a depth range of 50 to 200 cm (the C soil horizon) (Salminen et al., 1998).

2.2. Physico-chemical soil characterization

2.2.1. *Flemish soils*

All analyses were performed on air-dried and homogenized soil samples. In the Flemish samples, the concentrations of Fe, Al, Ni and Co were determined after microwave destruction of the sample with HCl, HNO_3 and HF and analyzed with ICP-AES (described in method CMA/2/II/A.3, Vito, 2005). The clay fraction (< 2 µm),was determined with the pipet method of Robinson-Köhn (according to method CMA/2/II/A.6, Vito, 2009a) and total organic carbon content (TOC) was analyzed by infrared detection after oxidation of organic carbon to CO_2 (according to method CMA/2/II/A.7, Vito, 2009b). pH was measured in a soil/KCl (1 mol/l) suspension with a liquid tot solid ratio of 5 (method CMA/2/II/A.20, Vito, 2008).

2.2.2. *European soil from the FOREGS Geochemical Baseline Mapping Programme*

Details about the analytical methods are provided in Sandström et al. (2006). "Soil samples were dried at 40°C, hammered to reduce agglomeration, disintegrated and homogenized in a porcelain mortar and passed through 2 mm sieve. Each sample was then split into three portions using a rotary divider, one of which was archived for further studies and the used for grain size analysis. The third portion was pulverized in a agate planetary mill to a grain size <0.063 mm, homogenized and divided into bottles to be submitted to the analytical laboratories."

The total organic carbon content of soil samples was analyzed using a LECO SC-DR144 instrument coupled to a Mettler AT 400 analytical balance. Grain-size distributions between 0.1 and 2000 µm were measured by a Laser Particle Sizer (LPS) technique using a Malvern Mastersizer 2000 instrument (Malvern, UK) equipped with a Hydro 2000G sample dispersion accessory. pH was measured in a soil/$CaCl_2$ (0.01 mol/l) suspension (device WTW pH90).

Total concentrations of a range of elements (SiO_2, TiO_2,Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5) was determined by wavelength dispersive x-ray fluorescence spectrometry (WD-XRFS) using Philips PW1480 and PW2400 WD-XRFs, with Cr and Rh anode x-ray tubes respectively.

In addition to the total concentrations of the elements, the acid leachable portion of selected elements (As, Ba, Co, Cr, Cu, Fe, Mn, Ni, Pb, S, V and Zn) was analyzed after hot aqua regia leach by ICP-AES, using a J-Y 70 Plus Geoplasma ICP-AES instrument. Samples were digested in aqua regia by weighing 1 g of sample in a polyethylene tube and adding 6 ml HCl and 2 ml HNO_3. The samples were left for 15 minutes at room temperature before heating in an aluminium block at 95°C for 60 minutes. After cooling, the samples were filtered and made up to 50 ml in a polyethylene flask (Salminen et al., 2005). Co and a range of rare earth elements (REE) and other trace metals were also determined on soil samples using a Perkin-Elmer Sciex Elan 5000 inductively coupled plasma mass spectrometer, after a complex sample destruction procedure, which is described as follows: "0.2 g of the soil sample was weighed into a Teflon dish and the organic material totally decomposed by evaporating the sample to dryness with 5 ml of 65% nitric acid, followed by the addition of 10 ml of 40% hydrofluoric and 4 ml of 70% perchloric acid and evaporated on a hot plate. The residue was dissolved in 20 ml of 8 mol/l nitric acid and 1 ml of 30% hydrogen peroxide before filtration. The filtrate was saved and the filter paper ashed in a platinum crucible. The residue was still fused with 0.2 g of lithium metaborate and 0.02 g of sodium perborate followed by dissolution in 5 ml of 0.8 mol/l nitric acid. The solutions were combined and made up to 100 ml in 1.8 mol/l nitric acid" (Sandström et al., 2006). This method is referred to as "Total multi-element determination by ICP-MS".

2.3. Statistical analysis

Statistical analysis was performed with the software package SPSS 20.0 for Windows.

Descriptive statistics (average, median, minimum, maximum, standard deviation and variance) were calculated for each variable. The 90th percentile of element concentrations in the upper soil layer of non-contaminated soils is often considered representative for the background value in soils (De Temmerman et al., 2003; Carlon, 2007). By comparing average and median values, soils with enrichment in Co can be detected (De Temmerman et al., 2003).

The normal distribution of the variables was checked by means of the Shapiro and Wilk test (W-test) and correlations between variables were assessed by calculating two-tailed Pearson correlation coefficients for the log transformed values. Multiple linear regression according to the stepwise method was

Topsoil (0-50 cm)							
	n	min	median	average	stdv	90 p	max
clay (%)	40	1.20	8.80	10.39	7.54	23.05	31.80
TOC (%)	40	1.41	4.40	4.82	2.24	8.53	10.70
pH	40	2.88	5.26	5.34	1.19	7.11	7.31
Al (mg/kg)	40	1930	9720	14408	11075	30630	42300
Fe (mg/kg)	40	1420	11400	15062	11452	30290	53300
Ni (mg/kg)	40	0.92	7.50	10.09	7.65	23.90	29.00
Co (mg/kg)	40	0.30	5.80	6.69	4.64	14.00	17.00
Subsoil (50-100 cm)							
	n	min	median	average	stdv	90 p	max
clay (%)	40	0.20	8.40	10.36	7.98	26.22	33.70
TOC (%)	40	0.22	1.02	1.32	1.03	2.41	5.13
pH	40	3.40	5.67	5.62	1.19	7.54	7.75
Al (mg/kg)	40	1790	11400	15870	12520	38110	50000
Fe (mg/kg)	40	1180	14450	17444	14406	33460	69000
Ni (mg/kg)	40	0.86	6.60	10.58	8.92	27.60	32.00
Co (mg/kg)	40	0.27	4.60	5.56	3.74	11.00	13.00

Table 3. Summary statistics for clay and total organic carbon (TOC) content, pH and total concentrations of Al, Fe, Ni and Co, based on Flemish data. n = number of samples, min = minimum; med = median; stdv = standard deviation, 90 p = 90th percentile of the dataset, max = maximum.

performed to deduce possible causal relationships between the variables (Webster, 1997, 2001). Attention was mainly paid to the possibility of predicting trace element concentrations in soil based on major element composition, pH, clay and organic matter content. Different assumptions of the linear regression (normality of the residues, autocorrelation, Quasi-Multicollinearity (QMC) and the Durbin-Watson coefficient) were tested.

3. Results

3.1. Total concentrations of Co in soils

Total Co concentration in the Flemish samples were in the range 0.30-17 mg/kg and 0.27-13 mg/kg in subsoil and topsoil samples respectively (Table 3).

Total Co concentrations in subsoil and topsoil samples from the FOREGS database are characterized by a right kurtosis, without outliers. Outliers were defined as data lying more than 1.5 interquartile range from the upper and lower quartile (Moore and McCabe, 2006). Normality of the dataset was tested by using the W-test (Shapiro and Wilck, 1965). Because the majority of the data (trace element and major element concentrations) showed a right kurtosis and were significant on the W-test, all the data except pH, were log-transformed.

In the FOREGS dataset, Co concentrations were in the range 0.50-255 mg/kg for topsoil samples and 0.50-191 mg/kg for subsoil samples (Table 4).

Total Co concentrations according to the "total multi-element determination by ICP-MS" were compared with the Co-content determined with "aqua regia hot plate destruction and ICP-AES determination" in the same set of samples, (Table 5). In the FOREGS database, the data in the tables containing the results from the aqua regia and total multi-element determination are not presented in exactly the same order and there are several missing samples for each of the methods. This inconvenience of the FOREGS database has also been mentioned by Lado et al. (2008). In order to be able to compare different determination methods, the data in the Excel sheets were rearranged, putting all data in the same order.

Topsoil (0-50 cm)							
	n	min	median	average	stdv	90 p	max
clay (%)	777	0.01	2.64	3.42	3.16	7.15	28.07
TOC (%)	816	0.07	1.73	2.48	3.18	4.57	46.61
pH	817	3.38	5.51	5.68	1.04	7.14	7.55
Fe (g/kg)	836	0.7	19.6	21.7	14.2	38	152.4
Ni (mg/kg)	836	1	14	30.68	123.98	40.4	2565
Co (mg/kg)	836	0.5	7	8.91	12.61	17	255
Mn (mg/kg)	836	5	382	524	540	1130	6483
Al_2O_3 (%)	845	0.37	11.03	10.48	4.46	15.97	26.67
Fe_2O_3(%)	845	0.16	3.51	3.80	2.34	6.67	22.3
Subsoil (50-100 cm)							
	n	min	median	average	stdv	90 p	max
clay (%)	748	0.01	2.60	3.72	4.14	7.89	39.48
TOC (%)	762	0.01	0.40	0.94	2.86	1.77	48.52
pH	762	2.89	5.79	6.01	1.02	7.44	7.86
Fe (g/kg)	788	0.7	21.05	23.22	14.30	40.97	94.2
Ni (mg/kg)	788	1	18	33.9	125.1	47	2586
Co (mg/kg)	788	0.5	8	9.5	10.3	17	191
Mn (mg/kg)	788	5	337	466	445	992	4387
Al_2O_3 (%)	788	0.21	11.74	11.24	4.82	17.01	27.12
Fe_2O_3(%)	788	0.11	3.75	4.05	2.32	7.06	15.58

Table 4. Summary statistics for total concentrations of clay and total organic carbon (TOC) content, pH, Fe, Ni, Co, Mn, Al_2O_3 and Fe_2O_3 based on the FOREGS data (Salminen et al., 2005) (Aqua regia determination for Co, Fe, Ni and Mn and XRF for Al_2O_3 and Fe_2O_3). n = number of samples, min = minimum; med = median; stdv = standard deviation, 90 p= 90th percentile of the dataset, max = maximum

Topsoil (0-50 cm)							
	n	min	median	average	stdv	90 p	max
Aqua regia	837	0.5	7.00	8.91	12.61	17.0	255
ICP-MS	843	1.5	7.78	10.42	13.26	19.2	249
Subsoil (50-100 cm)							
	n	min	median	average	stdv	90 p	max
Aqua regia	788	0.5	8.0	9.5	10.3	17.0	191
ICP-MS	791	0.1	9.0	11.1	10.5	20.0	170

Table 5. Summary statistics for total Co concentrations (in mg/kg), based on FOREGS data (Salminen et al., 2005) (Aqua regia determination and multi-element ICP-MS determination)

Based on a one sample t-test, it can be concluded that the average Co concentrations determined with both methods are not significantly different from each other ($p < 0.001$).

The scatter plots show a very good correlation between Co concentrations obtained with both methods (Fig. 2, FOREGS dataset). Co concentrations determined after aqua regia destruction were only slightly lower than Co concentrations determined after 'total multi-element determination'.

With both determination methods, Co concentrations in subsoil and topsoil samples from the FOREGS database are characterized by a right kurtosis and thus not normal distribution. Based on the boxplot, outliers were determined for the data from the FOREGS dataset: with the aqua regia determination, two outliers were identified (113 and 255 mg/kg in sample 39 and 231 respectively), whereas 4 outliers were determined when Co was analyzed with the ICP-MS method (102, 135, 78 and 249 mg/kg in samples 1, 39, 72 and 231 respectively). This example indicates that results are also determined by the analytical method and that, despite the fact that a relative good correlation is obtained between Co concentrations determined with both methods, different conclusions can be drawn from both analytical methods. When outliers were omitted from the dataset, no significant improvement in the relationship between both methods was observed (Fig. 2).

3.2. Relation of Co with other elements

3.2.1. Correlations

Concerning the FOREGS data, the correlation coefficients in Table 6 were calculated with the data from the aqua regia determination and from the XRF determination, since more elements that are relevant for this paper were measured with these methods compared with the total element determination

	Flemish dataset		**FOREGS dataset**	
	Topsoil	**Subsoil**	**Topsoil**	**Subsoil**
Co (ICP-MS)	-	-	0.903	0.904
Al_2O_3	0.571	0.761	0.548	0.546
CaO	-	-	0.223	0.087
Fe_2O_3	0.546	0.720	0.793	0.800
K_2O	-	-	0.146	0.097
MgO	-	-	0.689	0.616
MnO	-	-	0.790	0.722
Na_2O	-	-	-0.049	-0.013
P_2O_5	-	-	0.436	0.369
SIO_2	-	-	-0.308	-0.119
pH	0.268	0.224	0.328	0.169
S	-	-	0.275	0.166
clay	0.470	0.590	0.528	0.363
TOC	0.281	0.101	0.165	0.219

Table 6. Pearson correlation matrix showing the correlation coefficient of Co with the other variables analyzed in this study. All correlations were significant at $\alpha \leq 0.01$, except with organic carbon and pH (Flemish dataset) and with Na_2O and CaO for subsoil and Na_2O for topsoil (FOREGS dataset)

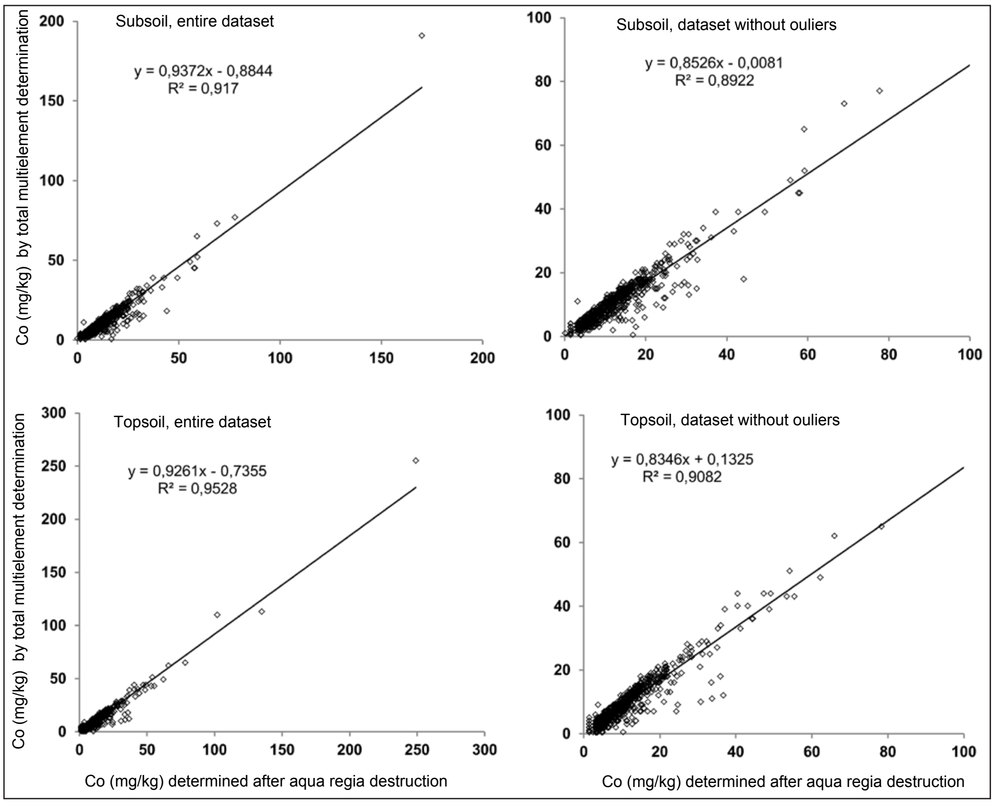

Figure 2. Comparison of the Co content is subsoil and topsoil samples (FOREGS dataset) as determined after "total multi-element determination" or with "aqua regia hot plate destruction", with and without outliers

with ICP-MS method. In general, Fe_2O_3 and MnO showed the strongest correlation with Co (Table 6).

3.2.2. Regression equations to predict Co concentrations in soils

In Flemish soil legislation, background values and soil remediation values for heavy metals are corrected for the clay content, organic matter content and pH of the soil (VLAREBO, 2006). Therefore, regression equations were first constructed using these 3 parameters as independent variables, both for the Flemish and FOREGS dataset (Table 7). For the FOREGS Subsoil data set, pH was not significant in explaining the variability in Co concentrations, whereas for the topsoil data, TOC was excluded from the regression equation because it was not a significant independent variable. For the Flemish topsoil and subsoil samples, only the clay content and organic carbon content were retained as independent variables

For both the Flemish and European data, the regression coefficients were low but they were significant (α =0.01 level) for the FOREGS subsoil and topsoil data.

In a second step, multiple linear regressions were performed with Fe_2O_3, MgO, CaO, K_2O, Al_2O_3, P_2O_5 and the clay (< 2µm fraction) and organic matter content as independent variables. pH, clay content (< 2µm fraction) and organic matter were included for the reasons mentioned before. Fe is a major component of Fe-(hydr)oxides, but is also a constituent of sheet silicates. In soils and sediments, Ca and Mg are dominantly found in sheet silicates when the parent material is Mg-rich (e.g. ultrabasic rocks) and in carbonate minerals (e.g. $CaCO_3$) in non-acidic soils.

Regression equations were constructed according to the stepwise method in order to only include the most significant independent variables.

Subsoil $\log(Co)= 0.698 \log(Fe_2O_3) + 0.404 \log(MnO) + 0.078 \log(clay) + 0.134 \log(MgO) - 0.105 \log(Na_2O) - 0.147 P_2O_5 + 0.777$ $R^2 = 0.776$

Topsoil $\log(Co)= 0.572 \log(Fe_2O_3) + 0.441 \log(MnO) - 0.152 \log(Na_2O) + 0.243 \log(MgO) + 0.107 \log(clay) + 0.658\ pH + 0.488$ $R^2 = 0.822$

The FOREGS datasets from the subsoil and topsoil samples were respectively characterized by 2 and 6 outliers, which were omitted from the regression equations in a second run. Omission of the outliers from the dataset resulted in a slightly better fit for the regression equations. Additionally, the QMC, homoscedasticity, normality of the residues and independent residues improved.

Subsoil $\log(Co) = 0.428 \log(Fe_2O_3) + 0.401 \log(MnO) + 0.084 \log(clay) + - 0.316 \log(K) + 0.168 \log(MgO) - 0.054 \log(Ca) - 0.138 \log(Na_2O) + 0.447 \log(Al_2O_3) -0.051 \log(TOC) + 0.777$
$R^2 = 0.800$

Topsoil $\log(Co)= 0.352 \log(Fe_2O_3) + 0.471 \log(MnO) - 0.158 \log(Na_2O) + 0.229 \log(MgO) + 0.106 \log(clay) - 0.125 \log(CaO) + 0.813\ pH + 0.479 \log(Al_2O_3) - 0.282 \log(K_2O) + 0.217$
$R^2 = 0.832$

Despite the high statistical significance of these regression equations, their significance in understanding the major parameters that control Co concentrations in soil is rather limited.

When only Fe and Mn are taken as independent variables, the following regression equations are obtained (dataset without outliers):

Subsoil $\log(Co) = 0.794 \log(Fe_2O_3) + 0.347 \log(MnO) + 0.841$
$R^2 = 0.785$

*Topso*il $\log(Co)= 0.704 \log(Fe_2O_3) + 0.586 \log(MnO) + 1.110$
$R^2 = 0.749$

		R^2	Regression equation
Flanders	Topsoil	0.225	= 0.112 + 0.534 log(clay) + 0.138 log(TOC)
	Subsoil	0.355	= 0.070 + 0.603 log(clay) + 0.117 log(TOC)
FOREGS	Topsoil	0.301	= -0.027+ 0.434 log(clay) + 0.810 pH
	Subsoil	0.158	= 0.810+ 0.226 log(clay) + 0.104 log(TOC)

Table 7. Regression equations for Co with clay content (defined as <2 µm fraction), TOC and pH as independent variables for the Flemish and FOREGS dataset.

For the Flemish dataset, a significant linear correlation (R^2 = 0.546 and 0.720, Table 6) was observed between Co and Fe, indicating that Fe would be a significant independent variable in the regression equation. Data on Mn concentrations in the soil samples were not available, so it was not possible to check whether the observations from Flanders fit well in the regression equation constructed with the FOREGS data.

4. Discussion

The considerable variability in total Co concentrations in the FOREGS database is related to differences in soil composition and lithology in the area that is covered by this database. Co concentrations in the Flemish and FOREGS database together are in the range 0.27 mg/kg - 255 mg/kg. The average Co concentration in the Flemish topsoil samples (6.69 mg/kg) is comparable to the concentration in the subsoil (5.56 mg/kg). In the FOREGS dataset, Co concentrations are on average 1.5 times higher in topsoil (8.91 mg/kg) and subsoil (9.47 mg/kg). On the maps representing the Co concentrations in topsoil and subsoil (Fig. 3), Flanders is located in a region characterized by lower Co concentrations in topsoil and subsoil, compared to other regions, such as Mediterranean Europe.

The maximal Co concentration in the FOREGS dataset is 255 mg/kg, whereas in the Flemish dataset, the highest Co content in a topsoil sample was 17 mg/kg. The highest Co concentration is found in Italy (255 mg/kg) and related to the ophiolitic bedrock.

In the European FOREGS dataset, "High Co values in soil are very often geogenic related to mafic or ultramafic rocks, but they can also be the result of adsorption and coprecipitation processes with Fe and/or Mn from lithologies rich in these metals (e.g. ferruginous sandstones, oolitic ironstones) and mineralization of siderite, goethite, haematite" (De Vos and Tarvainan, 2006). The natural occurrence of high concentrations of trace elements such as Co does not mean that the risk can be neglected and on locations where a potential and serious risk to the population is established, restrictions on land uses should be imposed (Armiento et al., 2011).

During the selection of the samples for the Flemish dataset, anthropogenic contaminated samples were eliminated from the dataset. The small difference in Co concentrations between topsoil and subsoil samples could be explained by atmospheric deposition of Co due to human activities.

Moreover, average Co concentrations (6.69 and 5.56 mg/kg respectively for topsoil and subsoil), are almost equal to the median values (resp. 5.80 and 4.60 mg/kg for topsoil and subsoil), which is an indication that outliers do not significantly affect the average value and that anthropogenic contamination with Co is probably not significant (De Temmerman et al., 2003). Background values, determined as 90th percentile values from the dataset, excluding outliers, were 11 mg/kg for subsoil samples, and 14 mg/kg for topsoil samples.

In the FOREGS dataset, background values of 17 mg/kg for both subsoil and topsoil were determined based on 90th percentile values for the aqua regia determination method, whereas values of 20 and 19 mg/kg were calculated for respectively the subsoil and topsoil dataset after total multi-element determination by ICP-MS.

In comparison with the norm values in several European countries (Table 1), these calculated background values are below these norm values, except for the 'negligible risk value' in The Netherlands. However, the total element content in soil provides only little information with respect to its potential and actual risk (Li et al, 2009). In this regard, taking into account soil parameters that are relevant for the retention and release of elements in soil offers a better way to evaluate element concentrations in soil.

In the present study, Fe and Mn were more significant than the clay content as explaining variables for the total Co content in soil. The attribution of the term 'clay fraction' to the < 2µm fraction is sometimes misleading. Besides clay minerals, Fe-rich minerals such as Fe-oxi/hydroxides and phylosillicates are often concentrated in the clay fraction (< 2µm) (Schulze, 1988). Instead of using the clay fraction as a parameter to explain trace element concentrations in soil and sediments, several authors followed a geochemical approach using the total concentrations of conservative elements to overcome these difficulties (e.g. Covelli & Fontalan, 1997, De Saedeleer et al., 2010, Ho et al., 2013). Our results suggest that normalization towards Fe and Mn is a useful approach to explain Co concentrations in soil.

For the soils in the FOREGS dataset, Fe, and Mn were the most significant explaining variables and several other studies indicate a strong relationship between the total content of Co and Fe and/or Mn. For example, Baize & Sterckeman (2001) also found a strong positive correlation between the Fe and Co content in soils in Northern France. In soil, Co has a high affinity for oxides of Fe and Mn and for clay minerals (Schuiling, 2003).

In an investigation of virgin soils in south-east Spain (Acosta et al., 2011), a clear relationship between total element concentrations and parent geological material was demonstrated, since cobalt was associated with Mg-bearing minerals such

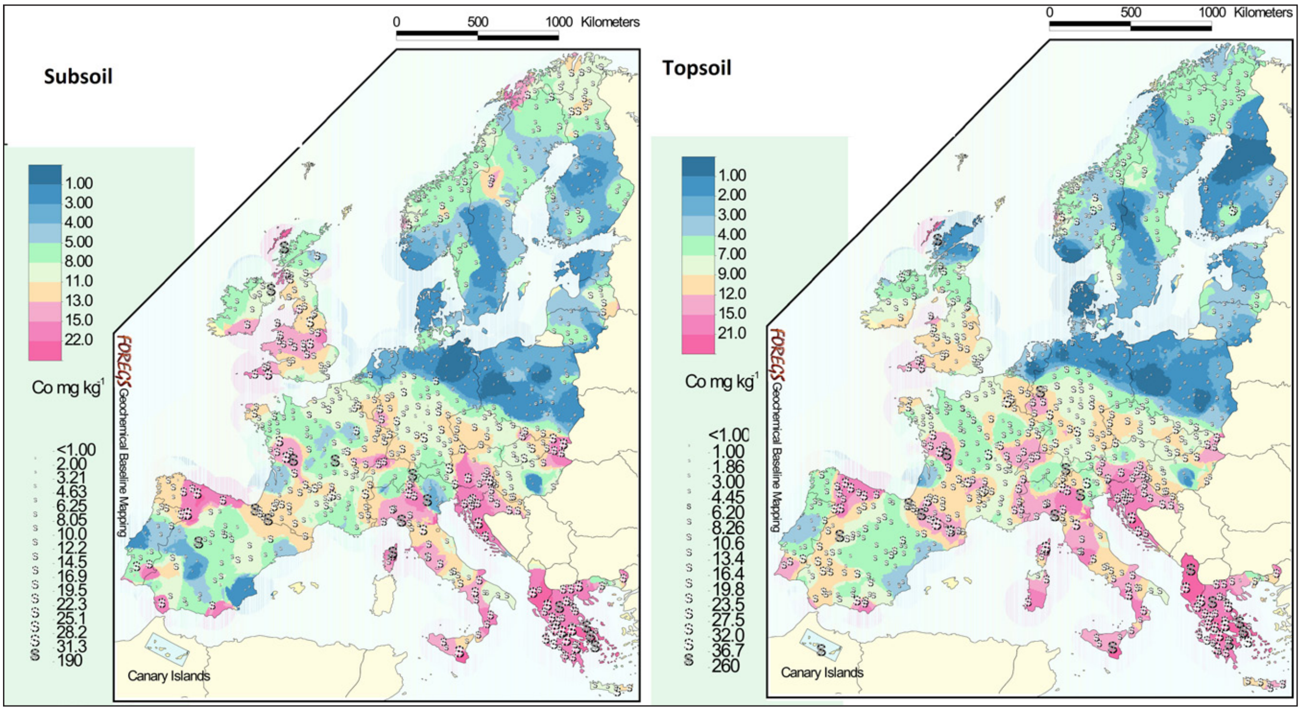

Figure 3. Maps of Co concentrations (as determined with the aqua regia method) in subsoil and topsoil (after Salminen et al., 2005)

as smectites. This was also reflected in correlations between elements in soil. Based on a Geostatistical analysis, Guillén et al. (2011) showed that Co in soil in the southwest of Spain was associated with the parent material (recent Holocene sediments over siliciclastic sediments deposited in marine and continental environments), with background values around 9.7 ± 0.7 mg/kg.

5. Conclusion

The Co content of the European soil samples (FOREGS database) was in the range 0.5 – 255 mg/kg, whereas in the Flemish data, Co concentrations between 0.27 and 17 mg/kg were found. Background values in the range 11-14 mg/kg were calculated. The higher Co values in soils in the southern part of Europe can be related to the occurrence of mafic or ultramafic rocks and lithologies rich in Fe and Mn. Moreover, regression equations with major elements, clay and organic matter content as independent variables were established in order to predict the Co content in soils. Fe_2O_3 and MnO were independent variables that most significantly explained the total content of Co in soil.

In the FOREGS dataset, several different procedures were used for the determination of total element concentrations in soils. It is clear that these procedures should be well-established, especially in large-scale studies, since this is essential to compare results of different studies and/or laboratories. However, in the case of Co, a very good correlation between Co concentrations was obtained with two different methods since Co concentrations determined after aqua regia destruction were only slightly lower than Co concentrations determined after 'total multi-element determination'.

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7. References

Acosta, J.A., Martínez-Martínez, S., Faz , A. & Arocena, J., 2011. Accumulations of major and trace elements in particle size fractions of soils on eight different parent materials. Geoderma, 161, 30-42.

Adriano, D.C., 2001. Trace Elements in Terrestrial Environments. Biogeochemistry, Bioavailability, and Risks of Metals, 2nd ed. 2001, XXIV, 867 p.

Armiento, G., Cremisini, C., Nardi, E. & Pacifico, R., 2011. High geochemical background of potentially harmful elements in soils and sediments: implications for the remediation of contaminated sites. Chemistry and Ecology, 27, 131-141.

ATSDR, 2004. Agency for Toxic Substances and Disease Registry. Toxicological Profile for cobalt. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

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.

Barceloux, D.G., 1999. Cobalt. Journal of Toxicology – Clinical Toxicology, 37(2), 201-216.

Barrow, N.J. & Whelan, B.R., 1998. Comparing the effects of pH on the sorption of metals by soil and by goethite, and on uptake by plants. European Journal of Soil Science, 49, 683-692.

Beak, D.G.; Kirby, J.K., Hettiarachachi, G.M.; Wendling, L.A.; McLaughlin, M.J. & Khatiwada R., 2011. Cobalt distribution and speciation: effect of aging, intermittent submergence, in situ rice roots. Journal of Environmental Quality, 40, 679-695.

Bjerrum N., 1936. Bjerrum's Inorganic Chemistry. 3rd Danish ed. Heinemann, London.

Brus, D.J., Lamé, F.P.J. & Nieuwenhuis, R.H., 2009. National baseline survey of soil quality in the Netherlands. Environmental Pollution, 157, 2043-2052.

Bølviken, B., et al., 1993. Final report of the Working Group on Regional Geochemical Mapping 1986-1993. Forum of European Geological Surveys (FORGES). Geological Survey of Norway (NGU) Open File Report 93.092.

Bölviken, B., et al., 1996. Regional geochemical mapping of Western Europe towards the year 2000. Journal of Geochemical Exploration, 56, 141-166.

Carlon, C. (ed.), 2007. Derivation methods of soil screening values in Europe. A review and evaluation of national procedures towards harmonization. European Commission, Joint Research Centre, Ispra, EUR 22805-EN.

Covelli, S. & Fontolan, G., 1997. Application of a normalization procedure in determining geochemical baselines, Gulf of Trieste, Italy. Environmental Geology, 30, 34-45.

De Saedeleer, V., Cappuyns, V., De Cooman, W. & Swennen, R., 2010. Influence of major elements on heavy metal composition of river sediments. Geologica Belgica, 13, 257-268.

De Vos, W. & Tarvainen, T., (eds), 2006. Geochemical Atlas of Europe. Part 2: Interpretation of Geochemical Mops, Additional Tables, Figures, Maps and Related Publications. EuroGeosurveys & Foregs, Espoo, Finland, 2006.

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.

Driessen, P.M. & Dudal, R. (eds), 1991. The major soils of the world. Lecture notes on their geography, formation, properties and use. Agricultural University of Wageningen and Katholieke Universiteit Leuven.

Dung, T.T.T., Cappuyns, V., Swennen, R. & Phung, N.K., 2013. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. Reviews in Environmental Science and Biotechnology, 12(4), 335-353, DOI: 10.1007/s11157-013-9315-1

Gil, C., Boluda, R., Ramos, J., 2004. Determination and evaluation of cadmium, lead and nickel in greenhouse of Almería (Spain). Chemosphere, 55, 27-34.

Guillén, M.T., Delgado, J., Albanese, S., Nieto, J.M., Lima, A. & De Vivo, B., 2011. Environmental geochemical mapping of Huelva municipality soils (SW Spain) as a tool to determine background and baseline values. Journal of Geochemical Exploration, 109, 59-69.

Hamilton, E.I., 1994. The geobiochemistry of cobalt. The Science of the Total Environment, 150, 7-39.

Ho, H.H., Swennen, R., Cappuyns, V., Vassilieva, V. & Van Tran, T., 2013. Necessity of normalization to aluminum to assess the contamination by heavy metals and arsenic in sediments near Haiphong Harbor, Vietnam. Journal of Asian Earth Sciences, 56, 229-239.

Horckmans, L., Swennen, R., Deckers, J. & Maquil, R., 2005. Local background concentrations of trace elements in soils: a case study in the Grand Duchy of Luxembourg. Catena, 59, 279-304.

Kabata-Pendias, A. & Pendias, H., 2001. Elements of group VIII. In Trace elements in soils and plants. CRC Press, Boca Raton, FL, 306-314.

Kapusta J.P., 2007. Cobalt Production and markets: a brief overview. Cobalt News, 07/1, January 2007, 9-12. Available from http://www.thecdi.com.

Lado, L.R., Hengl, T. & Reuter, H.I., 2008. Heavy metals in European soils: A geostatistical analysis of the FOREGS Geochemical database. Geoderma, 148, 189-199.

Li, H.F., Gray, C., Mico, C., Zhao, F.J. & McGrath, S.P., 2009. Phytotoxicity and bioavailability of cobalt to plants in a range of soils. Chemosphere, 75, 979-986.

McLaren, R.G., McKenzie, R.M., Lawson, D.M. & Swift, R.S., 1986. Sorption and desorption of cobalt by soils and soil components. Journal of Soil Science, 37, 413-426.

Micó, C., Peris, M., Recatalá, L. & Sánchez, J., 2007. Baseline values for heavy metals in agricultural soils in an European Mediterranean region. Science of The Total Environment, 378, 13-17.

Moore, D.S. & McCabe, G.P., 2006. Statistiek in de praktijk. Statistics in practice. Du, S. (ed.), The Hague, The Netherlands, 29-37.

Nieboer, E. & Richardson, D.H.S., 1980. The replacement of the non-descriptive term 'Heavy metals' by a biologically and chemically significant classification of metal ions. Environmental Pollution (Series B), 1, 3-26.

OVAM, 2001. Code van goede praktijk voor bemonstering van grond, grondwater, bodemvocht, bodemlucht en waterbodems. publicatienr. D/2001/5024/13, september 2001.

Provoost, J., Cornelis, C. & Swartjes, F., 2006. Comparison of soil clean-up Standards for trace elements between countries: why do they differ? Journal of Soil and Sediments, 3, 173-181.

Reid, R.L. & Horvath D.J., 1980. Soil chemistry and mineral problems in farm livestock. A review. Animal Feed Science and Technology, 5, 95-167.

Salminen, R. & Gregorauskiene, V., 2000. Consideration regarding the definition of a geochemical baseline of elements in the surficial materials in areas differing in basic geology. Applied Geochemistry, 15, 647-653.

Salminen, R. (chief-ed.), et al., 2005. Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps. Espoo, Finland: EuroGeosurveys&Foregs.

Salminen, R., et al., 1998. FOREGS geochemical mapping field manual. Geological Survey of Finland, Guide 47.

Sandström H., et al., 2006. Sample preparation and analysis. In Salminen et al., 1998. Geochemical Atlas of Europe. Part 1 - Background Information, Methodology, and Maps.

Schuiling, R.D., van Enk, R.J. & Bergsma, H.L.T., 2003. Natuurlijk voorkomen, mobiliteit en industrieel gebruik van "exoten" voorkomend in de Nederlandse bodem (Br, I, Ba, Sb, V, Sn, Co, Mo, Se). Retrieved from http://www.geochem.nl/.

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

Shapiro, S.S. & Wilk, M.B, 1965. An analysis of variance test for normality (complete samples). Biometrika, 52, 591-611.

Spurgeon, D.J., Rowland, P., Ainsworth, G., Rothery, P., Long, S. & Black, H.I.J., 2008. Gographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V and Zn) in British soils. Environmental Pollution 153, 273-283.

Tack, F.M.G., Verloo, M.G., Vanmechelen, L. & Van Ranst, E., 1997. Baseline concentration levels of trace elements as a function of clay and organic carbon contents in soils in Flanders (Belgium). The Science of the Total Environment, 113-123.

Vito, 2005. Compendium voor monsterneming en analyse (CMA) in uitvoering van het afvalstoffendecreet en het bodemsaneringsdecreet. CMA/2/II/A.3 Gesloten en semi-open microgolfoven destructiemethode met salpeterzuur, zoutzuur en waterstoffluoride, July 2005.

Vito, 2008. Compendium voor monsterneming en analyse (CMA) in uitvoering van het afvalstoffendecreet en het bodemsaneringsdecreet. CMA/2/II/A.20 pH in bodem, February 2008.

Vito, 2009a. Compendium voor monsterneming en analyse (CMA) in uitvoering van het afvalstoffendecreet en het bodemsaneringsdecreet CMA/2/II/A.6 Kleigehalte. (pipetmethode van Robinson-Köhn), December 2009.

Vito, 2009b. Compendium voor monsterneming en analyse (CMA) in uitvoering van het afvalstoffendecreet en het bodemsaneringsdecreet CMA/2/II/A.7 Totaal organisch koolstofgehalte (TOC), March 2009.

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

VMM (2013). Zware metalen in het grondwater in Vlaanderen [Heavy metals in groundwater in Flanders]. Vlaamse Milieumaatschappij [Flemish Environmental Agency]. Aalst, 96 pp.

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.

Wendling, L.A., Kirby, J.K. & McLaughlin, M.J., 2009. Aging effects on cobalt availability in soils. Environmental Toxicology and Chemistry, 28, 1609-1617.

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