

SOIL GEOCHEMISTRY IN AND AROUND THE TOWN OF MARCHE-EN-FAMENNE (WALLONIA, S-BELGIUM)

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(14 figures, 5 tables)

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ABSTRACT. The geological substrate of the town of Marche-en-Famenne, and its surrounding area, consists mainly of Givetian limestone and Frasnian to Emsian siliciclastics. The soil geochemistry within and around the town was studied by the collection of 214 samples from the urban area, and from a section of 3.5 by 20 km to the SW of the town. These samples were analysed for Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn by AAS. One of the most remarkable feature is that the contrast between limestone and sandstone is only weakly reflected in the major and trace element distribution patterns. This may be explained by the presence of loamy soils, which develop on limestone after weathering, which are very comparable to loamy soils developed on top of sandy shale and shale. A clear relation between geological substrate, soil-type and Fe-K-Ni content is apparent, and is also reflected in the bivariate correlation matrix. Further, red coloured lithologies of the so-called Burnotian age (i.e., Emsian) display an increase in Fe-content. Some particular dispersion patterns are clearly geogenetic in origin (e.g., in relation with mineralised faults, presence of overbank sediments, etc.), while in and around industrial sites, elevated heavy metal concentrations have been recorded and reflect an anthropogenic influence on the natural environment. Highest recorded Zn, Pb and Cd concentrations are respectively about 1300 mg/kg, 500 mg/kg and 4 mg/kg. However, values do not exceed trigger values, commonly used in environmental studies (e.g., Flemish Soil Sanitation Act). A speciation study, based on selective extraction, showed that about 20% of Zn and Pb are relatively easily dissolved; Cd can also potentially be leached, since more than 40% relates to the operationally defined "carbonate fraction". However, the Cd concentration is generally low. More important here is that overall heavy metals are dominantly bound to Mn- and/or Fe oxyhydroxides and to a fraction, which is only dissolved by strong acids ($\text{HCl}_{\text{conc}} - \text{HNO}_{3\text{conc}} - \text{HF}_{\text{conc}}$). This aspect, together with the absence of real anomalous concentrations in heavy metals, suggest that the eco- and human toxicological risk in the studied area is low.

KEYWORDS: environmental geochemistry, contamination, natural geochemical patterns, heavy metals, major elements

1. Introduction

Present-day policy on the regional and/or local level becomes increasingly confronted with environmental-contamination related problems. Politicians, as well as researchers, often face harmful situations created by historical carelessness. With respect to heavy metals, most of the sites with elevated contents are often wrongly linked to pollution created by historical industrial activities. However, such anomalies may be related to natural processes, which are used in exploration geochemistry for mineral prospecting purposes (Hawkes & Webb, 1962; Levinson, 1974; Rose et al. 1979; Thornton, 1995). Fur-

thermore, the fact that, on local and regional scales, elevated concentrations may be related to geological conditions, such as specific lithologies (e.g., Ni-Co-Cr anomalies above ultrabasic rocks; Turekian & Wedepohl, 1961; Turekian, 1977; Davy et al., 1999) or geochemical or physical dispersion mechanisms (e.g., placer deposits; Héral et al., 1999), illustrate that not all sites with elevated metal contents are related to anthropogenic pollution.

Nevertheless, once elevated concentrations of As, Cd, Cu, Co, Ni, Zn, Pb, etc., are detected in densely populated regions of industrial Western Europe, local habitants of-

ten react irrationally. Unfortunately, from the time of detection until the moment of a thorough assessment, with respect to the eco- and human toxicological risk, a period of several weeks or months can pass. This long time span leads to a general feeling of uncertainty, incapatownd and frustration among politicians, local habitants and researchers. This period is unfortunately regularly misused by unscientific discussions, whereby local politicians, as well as researchers, loose control of events (e.g., the polemic in Spring 2000 about the ISVAG furnace treatment plant in Wilrijk, Antwerp-Belgium).

It is, therefore, necessary that the government takes initiatives to recognise and thoroughly evaluate, within a reasonably short period, environmentally sensitive issues. In this respect, a systematic soil geochemical mapping of the present-day situation, in and around major towns, may be an important tool in policy-making. On these maps, locations or areas characterised by elevated concentrations are outlined in a systematic way. Anomalous areas are then ranked with respect to the need for follow-up research. A number of scientific tools exist, which can differentiate between elevated concentrations of natural and anthropogenic origin, and to assess their harm. Soil geochemical maps are, therefore, an important policy tool in planning and decision making.

The aim of the present study is to report on the soil geochemical mapping results in and around Marche-en-Famenne and its rural surroundings. In contrast to many other cities of the same size, especially in northern Belgium, the area under investigation is not considered to be industrially contaminated. This area was also selected, because of a varied geological substrate. The present study represents, therefore, a baseline mapping exercise, and the geochemical maps can serve as a reference framework against which future contamination may be evaluated. It is finally noted that the samples with elevated element concentrations were studied in more detail by sequential extraction.

2. Methodology

In and around the town of Marche-en-Famenne, a total of 214 soil samples were collected and analysed. Sample locations are shown on different maps presented herein (Figs. 5 to 13). The sampling grid was adjusted according to population density, i.e., a higher sampling density (16 samples/km²) in populated and industrialised areas, and a lower density (4 samples/km²) in forest and agricultural areas. The sampling grid was oriented SW-NE, and followed roughly the contact between Givetian carbonates and Frasnian siliciclastics. To increase representativity, at each pre-defined sampling point a composite sample was taken according to a star-like pattern (Fig. 1). This means that one sub-sample was taken at a pre-defined spot, while four additional sub-samples were collected from four directions perpendicular to each other at a distance of 20 to 100m. Care was paid to collect soil samples from geological substrates, and within areas of similar land use. At each spot the upper surface was removed (0-2cm), and a soil sample of approximately 1 kg weight was collected down to a depth of 15-20cm. Subsequently, these five sub-samples were well mixed by hand at the sampling location, and a composite sample of about 1kg was made. At each sampling location, a detailed description was recorded with regard to specific field conditions (e.g., land use, crop-type, forest-type, indications of anthropogenic disturbances, etc.), and sample specific features (e.g., colour, grain size, sorting, etc.).

Samples were dried at 40°C within 48 hours after sampling. Following sample splitting, about 0.2 kg of soil material was sieved to <125 µm, the fraction used for chemical analysis. Total dissolution was achieved with a strong acid attack (HCl_{conc} - $\text{HNO}_{3\text{conc}}$ - HF_{conc}). After evaporation and subsequent dilution with 2.5 N HCl and filtration, the elute was analysed for Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn by flame-AAS. Analytical precision was better than 10% for all elements at concentra-

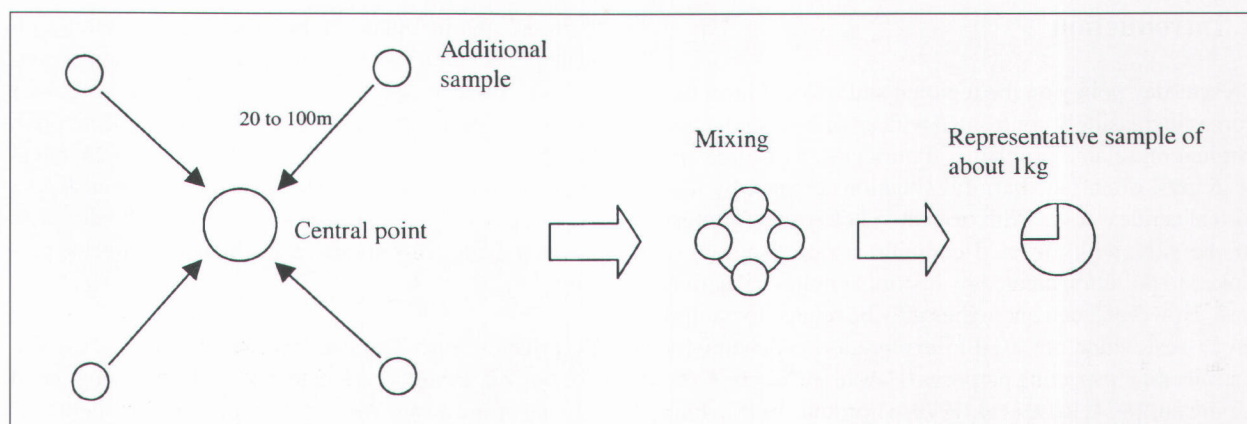


Figure 1. Sampling strategy

tions 3 times the detection limit. Most elements were above the detection limit, which is at the 1-2 mg/kg level. Only Cd concentrations were consistently near or below the detection limit of 0.5 mg/kg and precision was, therefore, low. For quality control purposes, duplicate analysis was performed on randomly selected samples, i. e. 10% of the samples were analysed twice. From this batch of samples, about 5% of replicate analysis was carried out on aliquots which were separately dissolved. Another 3% of these samples were taken twice in the field.

To be able to evaluate to which mineral phase some of the heavy metals relate, a selective extraction protocol was used. Although the mineral phases are operationally defined, they are able to give an estimate of element mobility. For this particular study a total of 10 samples was

selected. A slightly modified version of the Kersten and Förstner (1986) selective extraction protocol was used. It consisted of seven fractions: (i) water soluble fraction; (ii) ammonium-acetate soluble fraction at pH = 7 (considered to measure the absorbed and exchangeable fraction); (iii) Na-acetate fraction at pH = 5 (corresponding to the so-called "carbonate fraction"); (iv) hydroxylamine hydrochloride with $\text{HNO}_3(0.01\text{M})$ fraction at pH = 2 (interpreted in terms of Mn- and partially "amorphous" Fe-oxyhydroxides); (v) ammonium oxalate (0.2M) with oxalate acid (0.2M) at pH = 3 (dissolving amorphous and weakly crystalline Fe-oxyhydroxides); (vi) hydrogen-peroxide (30%) acidified with nitric acid (14M) at pH = 2 (dissolving organic matter and sulphides); and finally (vii) three concentrated acids dissolution, $\text{HCl}_{\text{conc}}\text{-HNO}_3\text{-HF}_{\text{conc}}$ (dissolving the final residue).

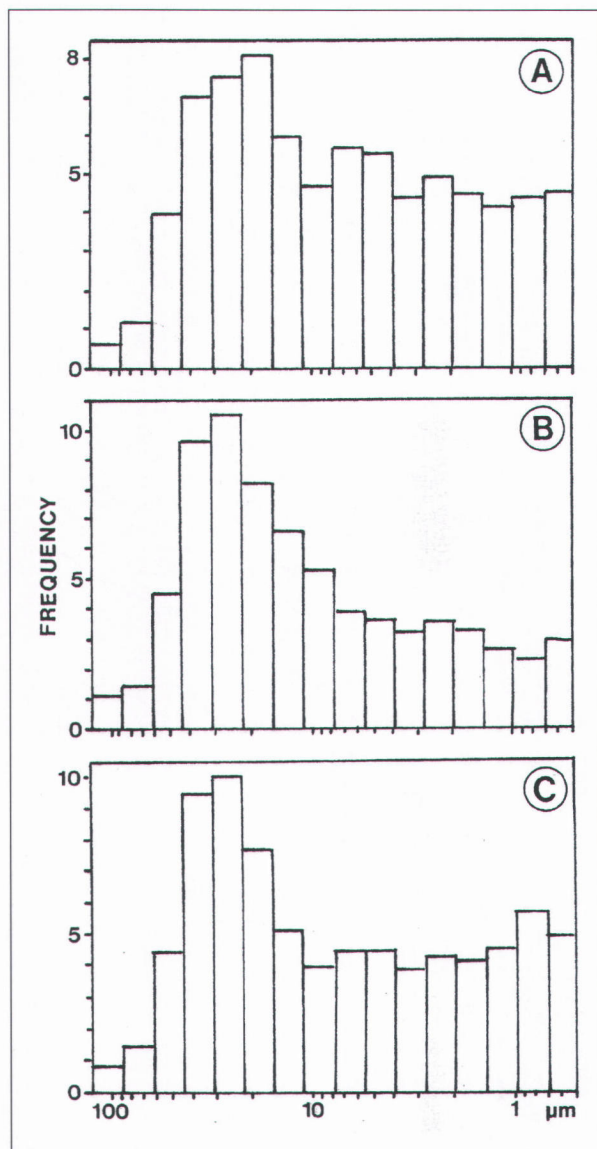


Figure 2. Examples of grain size distribution patterns (<125µm fraction) of representative soil samples taken in the Marloie area (above shaly lithologies; A and B; above limestone; C).

Organic carbon was determined on a set of 25 representative samples, according to the Walkley and Black method (Allison, 1960). Organic carbon content varied between 1.24 and 8.48%, with a mean value of 5.1% and a standard deviation of 1.9. Furthermore, on the same set of samples a granulometric analysis was carried out. It is noted that grain size analysis was performed on the <125µm fraction, since it was intended to investigate whether there are important areal or lithologically controlled variations. Since all samples were rather clay-rich, it was decided to use the sedigraph-method, because the laser granulometric method underestimates the clay fraction (Konert & Vandenberghe, 1997). Grain size analysis was carried out after decarbonation and removal of organic matter by hydrogen peroxide (30%). The <2µm clay fraction varied from 60 to 25%, with a mean value of 38.6% (standard deviation of 8.7). The 20-30µm fraction was the dominant grain size interval in nearly all samples, except the ones collected over limestone which were somewhat coarser grained (Fig. 2). Since variations were rather weak, a sample by sample grain size correction was not considered necessary, because the general soil geochemical picture, presented below, was not going to change noticeably.

3. Geological background

Sampled soils, within and around the town of Marche-en-Famenne and the villages of Marloie, Hargimont and On, are developed on Frasnian, Givetian to Couvinian (i.e., Eifelian) strata (Fig. 3). The latter formations generally display a N60°E strike and dip north. From NW to SE the following lithologies have been recognised (Vandeven, 1973): (i) nodular shale of Frasnian age (the nodular aspect relates to the existence of small carbonate nodules); (ii) dark to light-grey bioclastic limestone of Givetian age (locally some dolomite intercalations have been recognised); (iii) micaceous to sandy greenish coloured shale with thin limestone intercalations and carbonate cemented sandstone of Upper Couvinian (i.e.,

Eifelian age; (iv) fossil-rich grey-greenish coloured shale and carbonate-bearing shale with rare nodular limestone intercalations of Middle to Lower Couvinian (i.e., Eifelian) age; (v) sandy shale and micaceous sandstone of Emsian age. The latter is dominantly green coloured, however, sporadically it is limonite-rich and, consequently, red to red-brown coloured. Locally the so-called red-coloured "Burnot (i.e., Emsian) conglomerates" occur. It is also important to mention that along the "Wamme"- and "La Marchette"-river, alluvial terraces are developed. They mainly consist of limonite-rich gravel and of locally derived host rock fragments.

Some major longitudinal faults transect the area under investigation. Between Hargimont and Marloie, the

"faïlle d'On" borders the contact between Givetian limestone in the north and Couvinian (i.e., Eifelian) shale in the south (Fig. 3). The displacement along this steeply to weakly inclined south-dipping fault is in the order of 160m (Vandenvin, 1973). In the southern part of the study area the "faïlle de Lamsoul" occurs (Fig. 3). The displacement along this steeply southern dipping fault is in the order of 1125 to 1370m (Vandenvin, 1973). Along some of these longitudinal, and locally along transverse faults, minor mineralisation (pyrite, galena, sphalerite, chalcopyrite, etc.) has been reported (de Walque et al., 1976; Blondieau, 1993). However, no mineralisation is found in the sampled area, with the exception of a minor occurrence SE of the village of On (Fig. 3). Important mineralisation occurs just north of the village of On.

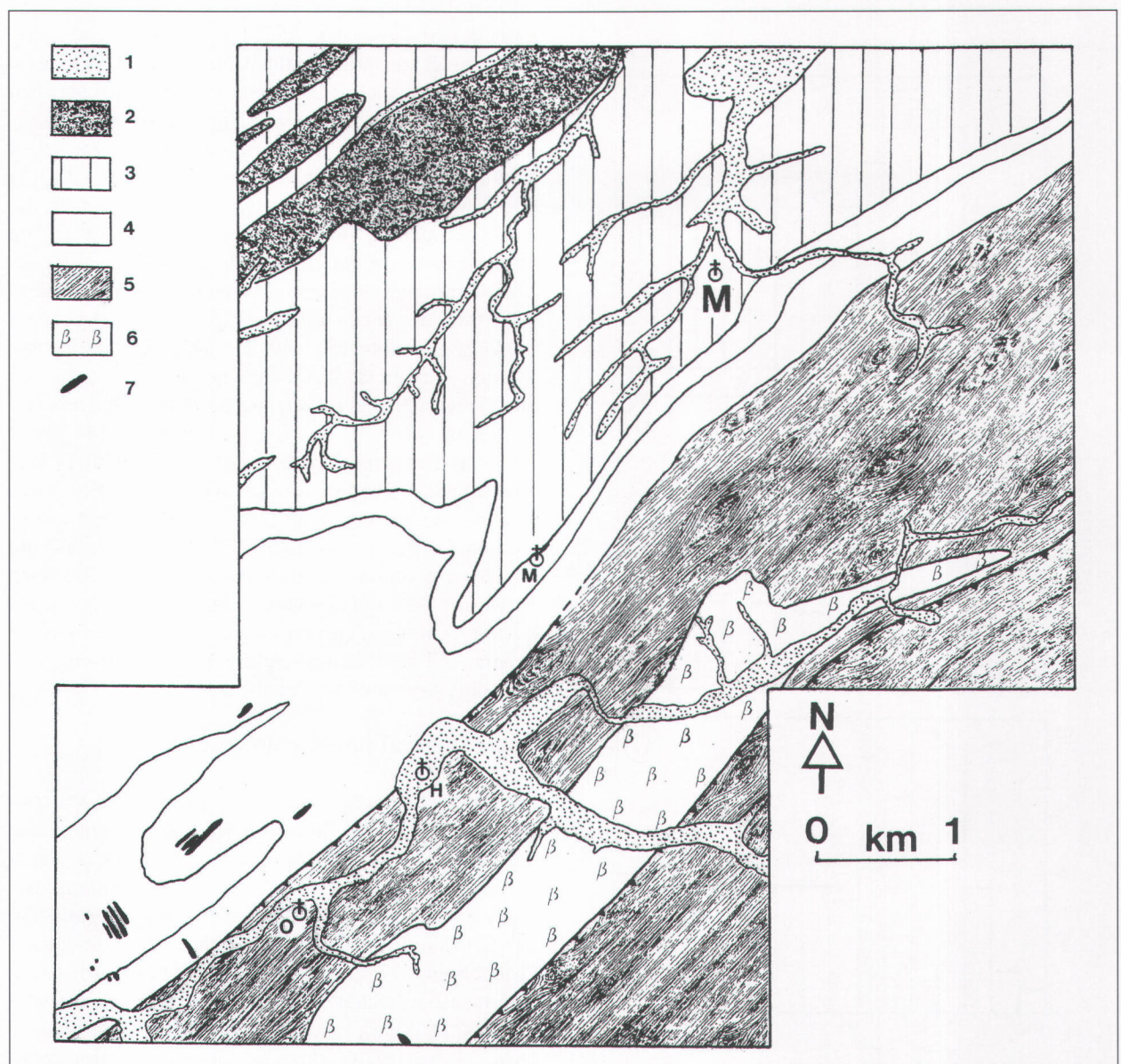


Figure 3. Simplified geological map of the study area; 1. Alluvial sediments; 2. Lower Famennian; 3. Frasnian; 4. Givetian; 5. Couvinian (i.e., Eifelian); 6. Burnotian (i.e., Emsian); 7. Fe-deposits; Large M = Marche-en-Famenne; small m = Marloie; H: Hargimont; O : On; Fault north of On = Faïlle d'On; Fault southeast of On = Faïlle de Lamsoul.

4. Soil geography

Soils in the study area are strongly influenced by the geological subsoil substrate. They are almost all stony-

loam soils, developed on shale or limestone (Dystric Cambisols and Eutric Cambisols respectively). Locally, aeolic-loess is present on which loamy soil is developed (Luvisols). Some soils have a high clay content

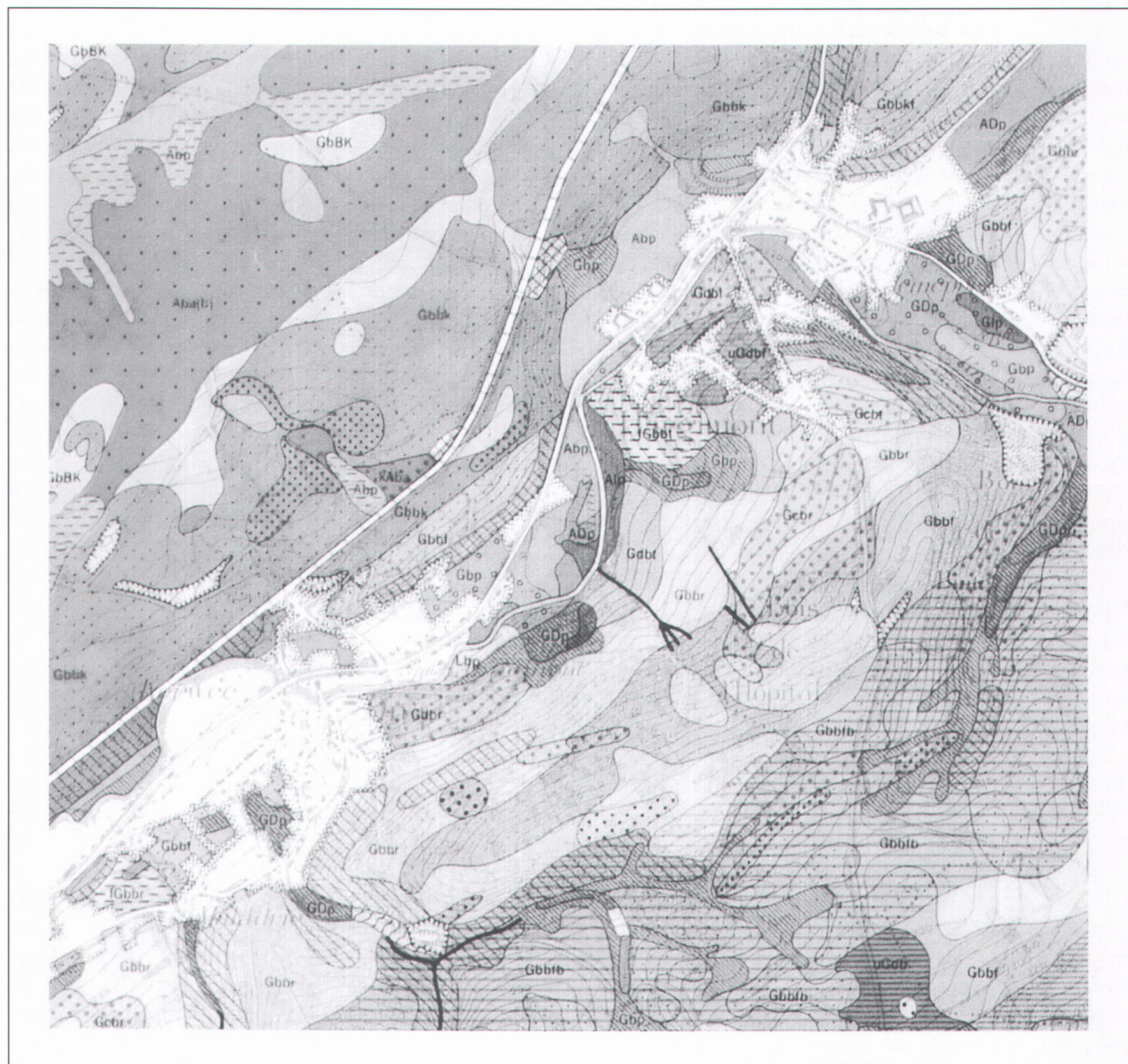


Figure 4. Raster image pedological map of the On - Hargimont area (Avril, 1973)

Soil-type Interpretation

<i>Lbp</i>	Sandy-loam soils
<i>Abp</i>	Loam soils
<i>Aba</i>	Loam soils with textural B horizon
<i>Gbp</i>	Soils on stony-loam material
<i>Gbbf</i>	Stony-loam soils with structural B horizon, containing shale fragments
<i>Gbbr</i>	Stony-loam soils with structural B horizon, containing shale and sandstone fragments
<i>Gbbk</i>	Stony-loam soils with structural B horizon, containing limestone fragments
<i>Gbbfb</i>	Stony-loam soils with structural B horizon, containing reddish shale fragments
<i>Gbbkf</i>	Stony-loam soils with structural B-horizon, containing fragments of shale and limestone
<i>fGbbr</i>	Stony-loam soils with structural B horizon, containing gravel and with a shale substrate beginning at shallow depth
<i>Gcbr</i>	Feebly gleyic, stony-loam soils with structural B horizon, containing shale and sandstone fragments
<i>uGbbr</i>	Moderately gleyic, stony-loam soils with structural B horizon, containing shale fragments, with a clay substrate beginning at shallow depth

attributable to shale-limestone weathering (Vertisols). Urban areas are evidently characterised by non-natural soils (Urbic Anthrosols, "Hortisols", etc.). In the following paragraph, the Belgian soil classification system is used. In Figure 4 the general pedological outline is given for the area between the villages of On and Hargimont. The latter is based on the Belgian soil map (Avril, 1973). It is noted that no detailed pedological map exists for the town of Marche-en-Famenne and its neighbourhood. Therefore, interpretation of soil-types in the latter area is based on the link between pedology and geology, as observed in adjacent regions around the town of Marche-en-Famenne.

Soils in the On-Hargimont area are almost all stony-loams, developed on shaly lithologies or limestone. From Figure 4, one can recognise large local variations. In the area westwards of the railroad (line Rochefort - Marche-en-Famenne), one finds loamy soils with a textural B horizon (*Aba*), and stony-loams with a structural B horizon, containing limestone fragments due to Givetian calcareous subsoil (*Gbbk*). To the east of the railroad, soils of plateau and slopes are mainly developed on shale and sandstone of Middle Devonian Eifelian (formerly Couvinian) stage. They are mainly stony-loam soils with a structural B horizon and contain either fragments of shale (*Gbbf*) or shale and sandstone (*Gbbr*). Also, reddish shale fragments of Lower Devonian Ems stage (*Gbbfb*) (formerly Burnotian) have been reported. Soils of valleys and depressions are either loamy (e.g., *Abp*) or stony-loams (e.g., *Gbp*).

The subsurface to the north-west of Marche-en-Famenne is dominated by Upper Devonian Frasnian strata. The inferred soils that develop upon this parent material will be stony-loams with a structural B-horizon, containing fragments of shale and limestone (*Gbbkf*). In the (south) east of the study area similar calcareous subsoils, but containing limestone fragments (*Gbbk*), are assumed to have developed upon Givetian strata. Further south, the latter geological formation is frequently covered with Quaternary calcium-poor loam sediments (i.e., q1n, limon non ossifère) on which loamy soils with a textural B horizon (*Aba*) are developed. In the easternmost section of the study area the same shale and sandstone of the Eifelian (formerly Couvinian) stage (Middle Devonian), as in the On-Hargimont area, are found. Consequently, *Gbbr*- and *Gbbf*-soils will also be present in this area.

5. Results

5.1. Relation between major elements and geology/pedology

In Figures 5 to 13 the most relevant soil geochemical maps are presented. With regard to the distribution of Ca (Fig. 5) and Mg, it was expected to see a reflection of the subsurface geology. This is partly deducible from its distribution, especially in the southernmost part of the study area (Hargimont - On), where the highest contents in Ca and Mg correspond to soils developed upon calcareous shale and carbonate-bearing lithologies of Upper Couvinian (i.e., Eifelian) age, on which dominantly *Abp*-soils occur (Fig. 6A). The absence of elevated Ca and Mg concentrations between On and Hargimont is due to the presence of overbank sediments. Further, in the area between Marche-en-Famenne and Marloie, elevated Ca and Mg values have been recorded over nearly the entire area, due to the existence of calcareous soils (both *Gbbkf*- and *Gbbk*-soils). A striking feature exhibited by the Ca-Mg distribution maps is the elevated concentrations, which occur in urban areas and along roads. This is well-pronounced in the neighbourhood of Marche-en-Famenne. The Mg-pattern even becomes erratic. A possible interpretation is the addition of Ca and Mg on top-soils by human activities, e.g., dumping of Ca-Mg-bearing building materials, etc. However, elevated concentrations do not systematically occur in urban or industrialised areas, as observed by the relatively low levels in Marloie (Fig. 5). It is noted that Schrap and Baumgarten (2000) also recorded that soils in inner town areas are characteristically enriched in carbonates and have high pH-values.

With respect to Fe (Fig. 7), the highest concentrations occur in the sector north of Marloie and west, north and east of Marche-en-Famenne, and in the region south of Hargimont (Fig. 6B). The highest values, in the latter area, correspond specifically to locations where fragments of red-coloured shale occur in *Gbbfb*-type soils. This is clearly related to the presence of Fe-oxides. Also, *Gbbf* and *Gbbr* soils display high Fe-concentrations, which are higher than those observed within *Abp* soils. Further, Mn displays elevated contents in the latter area. The presence of Fe- (and Mn)-oxyhydroxides explains these high concentrations with values for Fe >3%. High Fe-values in the north-



Figure 5. Soil geochemical distribution map of Ca (major sampling grid)

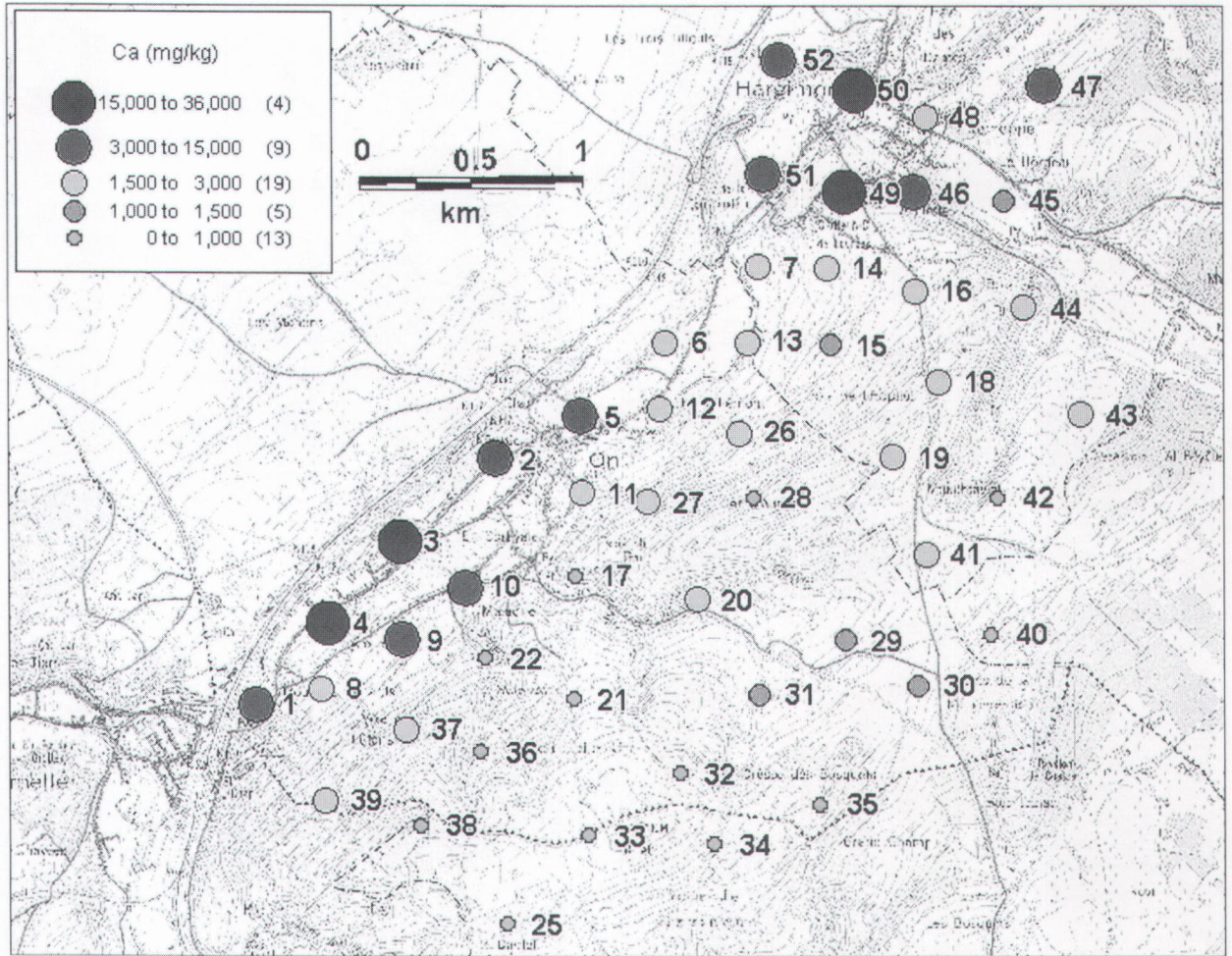


Figure 6A. Soil geochemical distribution map of Ca (detailed sampling grid of On - Hargimont);

ern part of the study area, between Marche-en-Famenne and north of Marloie, are correlated to high K-concentrations (Fig. 8), suggesting that a relationship exists with *Gbbkf*-type soils containing shale fragments. Actually, in many geochemical studies potassium is used as an indicator for clay in areas where the clay mineral is illite (Swennen & Viaene, 1981). It is important to mention here that Mn does not display elevated concentrations in this area, as observed south of Hargimont. Only some erratically distributed high Mn locations occur, where no clear interpretation can be given. South of Hargimont, the Fe-K covariance also does not exist, an observation which concurs with other subsurface geology and soil development features.

5.2. Relation between heavy metals and geology/pedology

With respect to the heavy metal trace element distribution it can be stated that very high concentrations are rather rare. Only four soil samples display levels between 1000 and 1400 mg/kg for Zn, and six locations

with Pb-concentrations exceeding 300 mg/kg exist with a maximum of 510 mg/kg. Copper and Ni values do not exceed 200 mg/kg.

In general terms, there is no clear relationship between heavy metal distribution and soil-type or geological subsurface, with the exception of Ni (Fig. 9). For this element the area southwest of Marche-en-Famenne displays systematically higher values than elsewhere. These elevated concentrations could be related to *Gbbkf* soil-type developed above Upper and Middle Frasnian strata, which also explains the covariance with Fe and K.

The highest Pb, Zn and Cu concentrations are recorded in urban or industrialised areas (Figs. 10, 11 and 12), whereas in most agricultural and forested areas levels are low and comparable to normal local background values (see discussion below). The clearest pattern is exhibited by the Pb distribution, where values >100 mg/kg occur in parts of the built-up areas of Marche-en-Famenne, Marloie, Hargimont and On (Figs. 10 and 13A). At first glance, it seems that mainly the oldest parts of the town display these somewhat elevated contents. However, these older town-parts have also low, background-like,

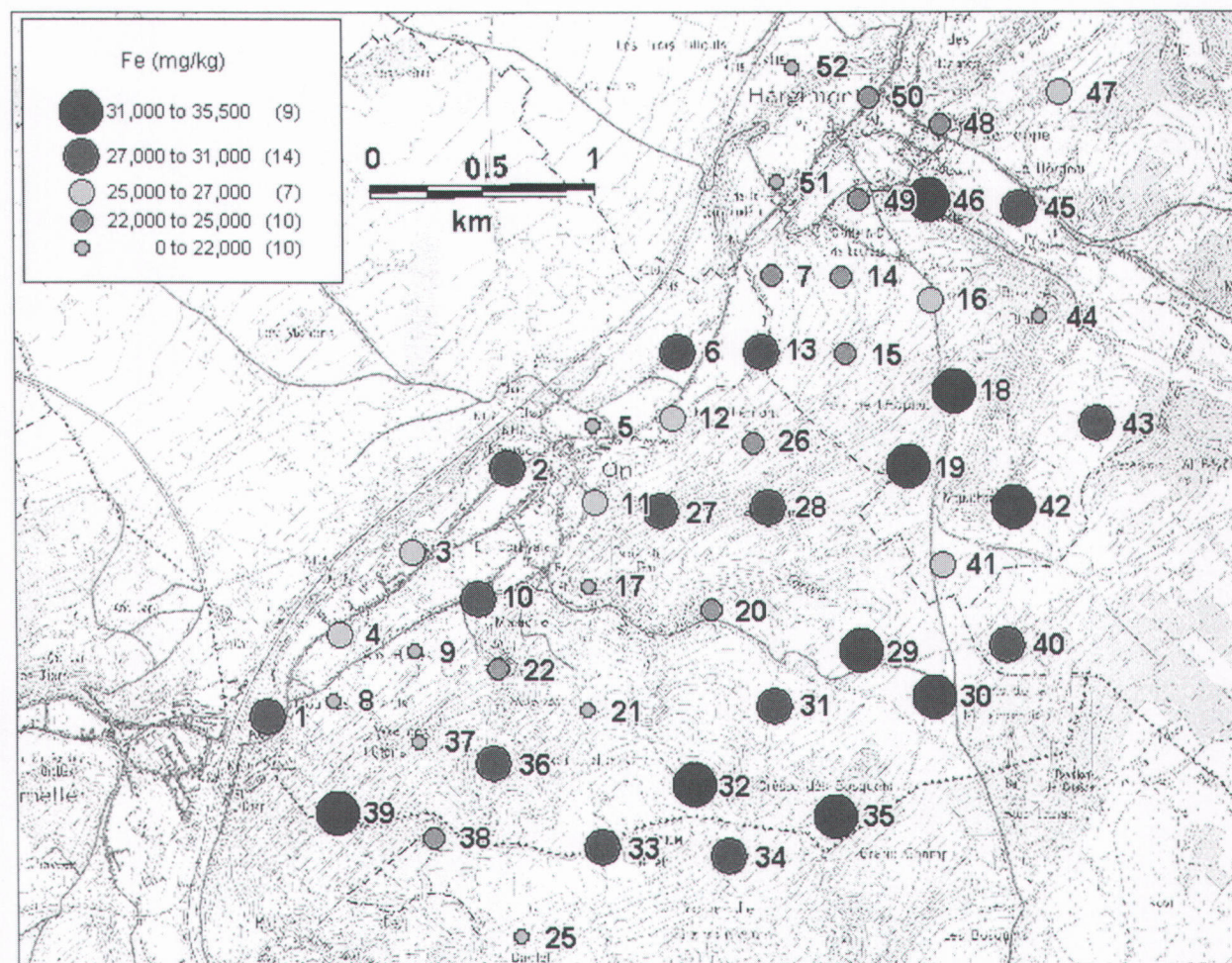


Figure 6B. Soil geochemical distribution map of Fe (detailed sampling grid of On - Hargimont)

concentrations. For Zn and Cu the distribution pattern is less clear, but still sampling locations, with the highest concentrations, exclusively occur in residential areas (e.g., Marche-en-Famenne, Marloie-nord; Figs. 11 and 12). These general patterns suggest that anthropogenic activities may be responsible for this increase in heavy metal contents in urban and industrialised areas. This may be related to different activities, like the past use of leaded petrol, use of Zn, Pb, Cu-containing metals in building materials and wires, paints, etc.

It is worth noting that some sampling points clearly deviate from the general element distribution patterns. For example, elevated Pb-concentrations have been recorded in Bois du Ban (east-south-east of On), far away from common anthropogenic activities (Fig. 13A). The fact that these elevated values follow an east-north-east trend, with increasing concentrations oriented towards the combustion-furnace of the limestone quarry north-east of Hermelle, suggests that a relation with the combustion activities may exist. The local population reports that during some periods in the year, a black dust is deposited, which is derived from the burn-

ing of tyres, used as additives for combustion. Whether the latter is true could not be investigated, but it is known that rubber tyres contain elevated Pb, but also Zn concentrations (Clarit, 1997). However, samples taken at Bois du Ban do not have elevated Zn contents. Therefore, the origin of the elevated Pb-concentrations is not clear.

Along the railroad from Ciney to Arlon near Pelaimont (3 km south-east of Marche-en-Famenne) one soil sample has a Cu-content of 174 mg/kg. By chance this was one of the sample locations where a replicate soil sample was collected. The second sample has only a concentration of 66 mg/kg Cu, but its Zn content is 1213 mg/kg compared to only 245 mg/kg of the first sample. It is, therefore, likely that at this site a very local contamination, possibly of particulate nature, causes these anomalous values.

Finally, as mentioned in the geological section, south of On there occurs minor mineralisation. At this locality a somewhat higher Zn-value (i.e., 125 mg/kg; Fig. 13B, sampling point 33) was recorded, which may be related



Figure 7. Soil geochemical distribution map of Fe (major sampling grid)

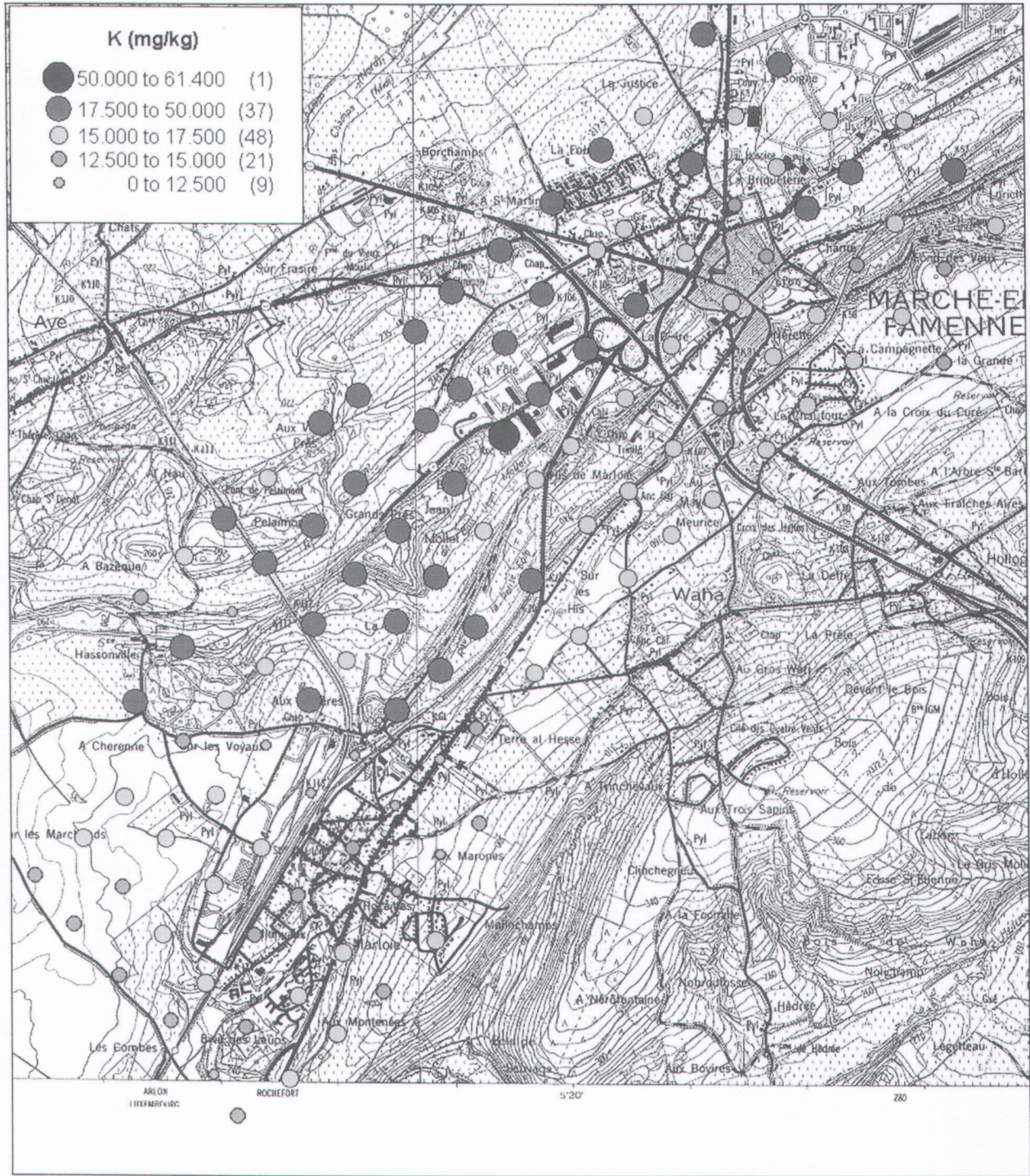


Figure 8. Soil geochemical distribution map of K (major sampling grid)



Figure 9. Soil geochemical distribution map of Ni (major sampling grid)



Figure 10. Soil geochemical distribution map of Pb (major sampling grid)



Figure 11. Soil geochemical distribution map of Zn (major sampling grid)



Figure 12. Soil geochemical distribution map of Cu (major sampling grid)

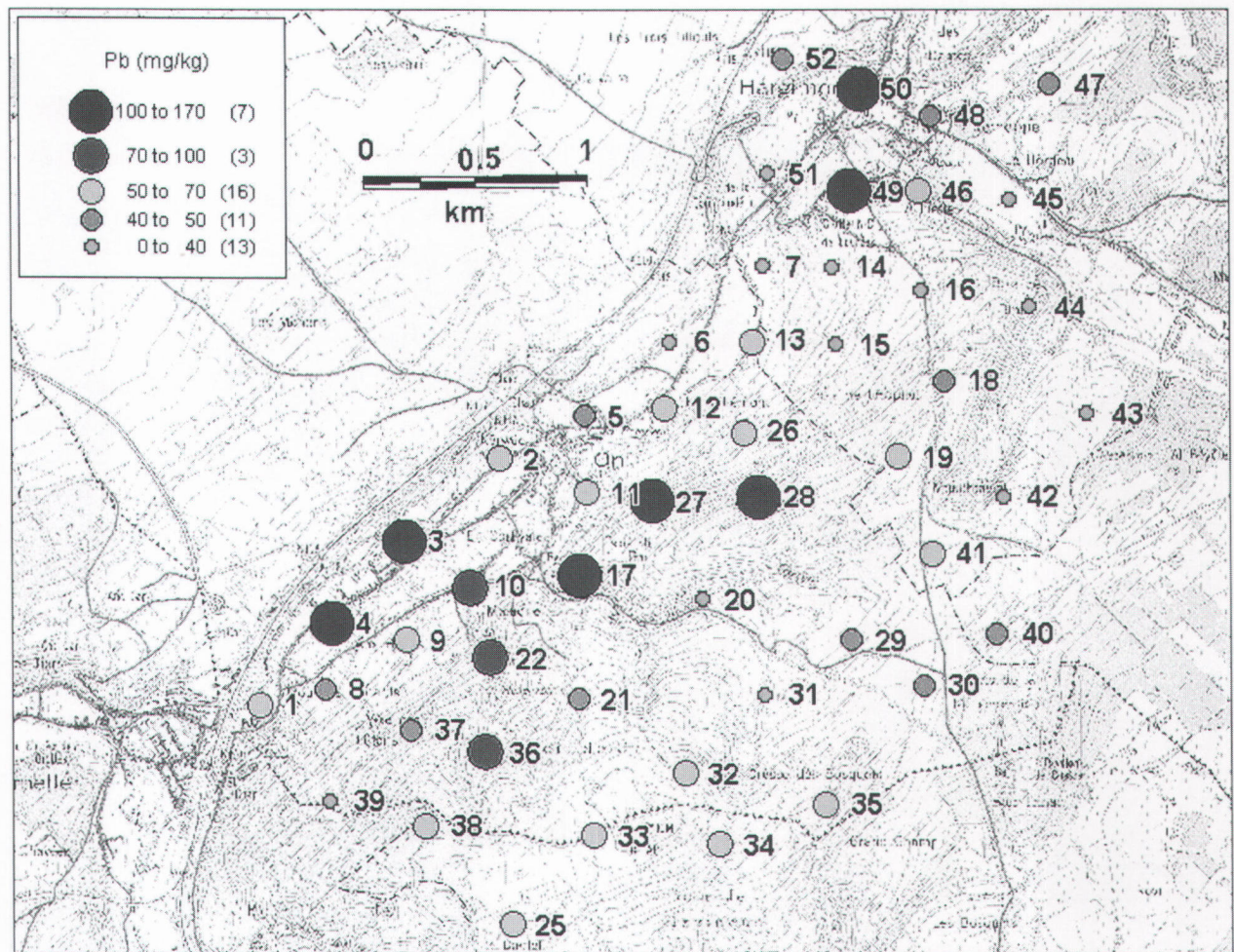


Figure 13. A = Soil geochemical distribution map of Pb (detailed sampling grid of On - Hargimont);

to the reported mineralisation. It is noted, however, that other heavy metal values are within the normal background range (Fig. 13A). This contrasts, to some degree, to a sample taken about 1km east of the mineralised location, i.e., in "Brèsse des Bosquets" (Fig. 13A, sampling point 35). This composite soil sample has somewhat elevated concentrations for Zn, Cu, Ni and Co, when compared to values recorded in the surrounding forested area (i.e., 155, 47, 47, 55 mg/kg respectively). The origin of these comparatively elevated concentrations is unknown, but it could be related to concealed mineralisation.

6. Statistical analysis

Mean values and other statistical parameters of the entire raw dataset ($n = 214$) are reported in Table 1. Histograms show that most elements display a lognormal distribution. Therefore, the dataset was log-transformed before Pearson's product moment correlation was calculated. A number of significant correlations are shown by the correlation matrix (Table 2). A strong Zn, Cu, Pb cluster develops, which henceforth will be described as

the heavy metal cluster. Additionally, an Fe, Ni, Mg, K or lithology cluster is present. Calcium is linked to this cluster by its strong correlation with Mg. It was expected, however, that Ca would be entirely integrated into the lithology cluster, but this is not the case. A possible explanation is the absence of high Ca-concentrations in Fe, Ni, K-rich soils. Calcium is also correlated with the heavy metal association through Pb, which displays elevated contents in areas with human activities. Therefore, the anthropogenic influence may, to some degree, be explained by the geochemical pattern, whereby elevated heavy metal concentrations are correlated with soils having increased Ca and Mg contents. This is an important observation, since these soils often have a high pH (Schraps & Baumgarten, 2000), which implies low heavy metal mobility.

There are important regional statistical variations, which will not be discussed in detail here because it is difficult to define uniform criteria to differentiate sample populations. It is clear that geochemical dispersion patterns are controlled by complex processes, whereby different populations have been mixed. The latter feature

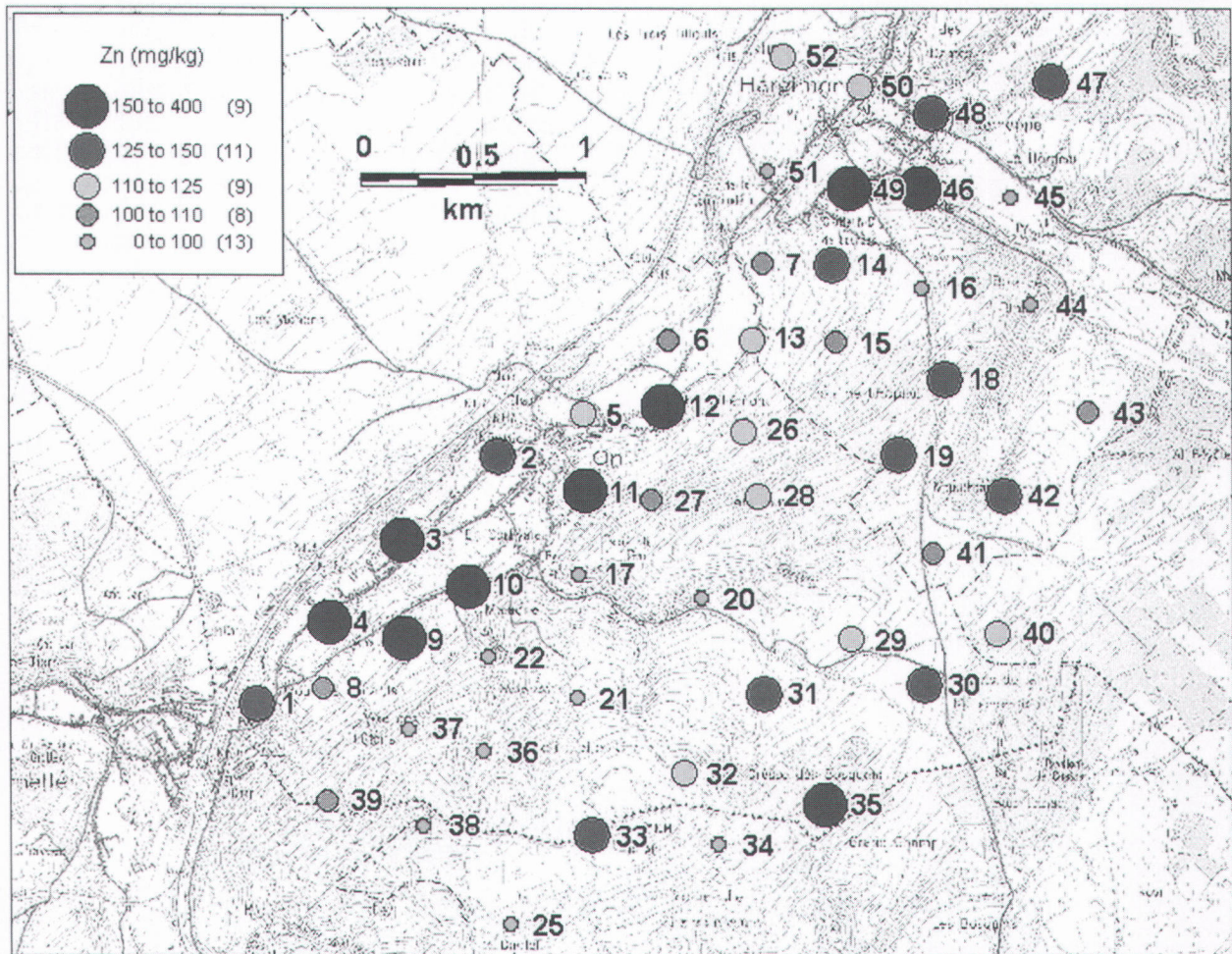


Figure 13.B = Soil geochemical distribution map of Zn (detailed sampling grid of On - Hargimont)

refers to specific soil-types for example, or the existence of “natural” dispersion patterns, and those that are anthropogenically altered with respect to their heavy metal and Ca-Mg contents. It was, therefore, decided not to discuss in detail the statistical analysis results.

7. Comparison with other datasets and reference values

A comparison of major elements with other data reported in the literature is not necessarily meaningful, since geochemical distributions are normally linked to soil-type and geological substrate. However, a comparison of measured and reported trace element contents is more interesting. In Table 3 intervention values of different legislative bodies, as reported in the website of the Walloon government, are listed (Office Wallon des Déchets, 1999). Despite the criticism that can be made about the derivation of these data, e.g., no corrections made for clay and organic matter content for example, they can be used in a preliminary evaluation. Furthermore, if the existing Flemish reference system (OVAM, 1996) is applied on the 25 samples, where granulometric

and organic matter measurements have been carried out, then in none of the randomly chosen cases the intervention values for agricultural soil are exceeded. Even the highest concentrations recorded for Zn and Pb do not generally exceed these intervention values, if corrections for clay and organic matter content are taken into account.

In a soil geochemical study, carried out around the mineralisation of Heure, de Walque et al. (1976) concluded, on the basis of sample population distributions that values of Zn >251 mg/kg and Pb >132 mg/kg correspond to levels delineating mineralised and historically mined areas. Values below these limits are considered to reflect the so-called “normal local background” pattern. Taking into account these values, it is concluded that a rather large number of samples in the present study have moderately high concentrations (i.e., 20% for Zn and 13% for Pb). The Cu, Ni and Co concentrations recorded in this area are of the same order of magnitude as those reported by de Walque et al. (1976). However, several of the values recorded in this study, especially for Cu and Ni, are higher than those reported in the mineralised area.

Statistical parameters	Ca	Fe	Mg	K	Mn	Ni	Zn	Cu	Pb
Minimum	224	13398	829	7487	73	30	52	10	30
Maximum	214466	46653	9574	61398	2251	192	1373	181	510
Mean	17576	27341	4004	16084	848	56	205	35	88
Standard Dev	24393	6119	1711	4154	323	16	193	26	72

Table 1. Mean values and other statistical parameters (in mg/kg) of the soil geochemical data (number of samples = 214)

	Ca	Fe	Mg	K	Mn	Ni	Zn	Cu	Pb
Ca	1								
Fe	-0.034	1							
Mg	0.477	0.462	1						
K	-0.023	0.478	0.279	1					
Mn	-0.106	0.214	-0.196	-0.112	1				
Ni	0.126	0.638	0.526	0.342	0.063	1			
Zn	0.263	0.151	0.320	-0.099	0.072	0.293	1		
Cu	0.244	0.254	0.370	-0.001	0.065	0.374	0.715	1	
Pb	0.315	0.113	0.292	-0.088	0.066	0.235	0.647	0.632	1

Table 2. Pearson's product moment correlation coefficient based on the 214 samples analysed in this study

Element	Dutch list		Canadian list *			Eikmann-Klocke list			Flemish list		
	C	New values	AZ	RZ	IZ	AZ	RZ	IZ	AZ	RZ	IZ
As	50	55	20	30	50	50	60	200	45	110	300
Cd	20	12	3	5	20	5	10	20	2	6	30
Cr total	800	380	75	250	800	500	500	800	130	300	800
Cu	500	190	50	100	500	200	200	2	200	400	800
Hg	10	10	2	2	10	50	50	50	10	15	30
Ni	500	210	50	100	500	200	200	500	100	470	700
Pb	600	530	50	300	600	1000	2000	2000	200	700	2500
Zn	3000	720	100	500	1500	600	600	3000	600	1000	3000

AZ: Agricultural zone

RZ: Residential zone

IZ: Industrial zone

* Quebec

Table 3. Intervention values (in mg/kg) used by the Walloon Government (Office Wallon des Déchets, 1999)

Van der Sluys et al. (1997) study on the geochemistry of pre-industrial background values in the area is deduced from old overbank deposits, and their data for the river Lomme near Rochefort, and the river Ourthe at Hotton are given in Table 4. One of their conclusions is that in agricultural and forested areas measured element concentrations are within the expected variation, as found in samples interpreted as pre-industrial overbank sediments. However, in residential and industrial areas, recorded values often exceed reported pre-industrial ones in overbank sediments by a factor of 2 to 3. A likely explanation is that most of these samples reflect an anthropogenic overprinting.

Element	Rochefort	Hotton
Ca	2573	1644
Cd	2.3	2
Cu	17	20
Fe	30076	33573
K	13911	15899
Mg	4281	5909
Mn	1395	387
Ni	45	45
Pb	27	28
Zn	94	91

Table 4. Geochemical characteristics (in mg/kg) of two pre-industrial overbank sediments reported in Van der Sluys et al. (1997)

Finally, in Table 5 trace element concentrations from "natural" Belgian top soils, which are related to soil texture are reported (Temmerman et al., 1982). These authors describe elevated concentrations of Mn, Hg, Ni, and to a smaller extent of As and Zn, in stony-loam soils (textural class "G"; for explanation of abbreviations see Table 5) compared to "normal" loam soils (textural class "A"), especially when the soil is shallow and developed on and/or mixed up with shale. Clay- and heavy clay-soils (respectively textural classes "E" and "U") are generally enriched in most heavy metals (Table 5). It is interesting to note that if data from this study are compared with those reported in Table 5, an enrichment in heavy metals in residential and industrialised areas becomes apparent.

8. Results of the selective extraction

As expected the selective extraction of Fe indicates that in general a proportion of 30-40% is related to crystalline Fe-oxyhydroxides, while the rest is held by the least soluble phases, e.g., most likely Fe-bearing silicates. It was expected that Mn-bearing phases will exhibit a similar pattern. However, the picture is more complicated since, in general, about 40% of Mn is bound to the relatively easily dissolved Mn oxyhydroxides and partially "amorphous" Fe-oxyhydroxides; about 30% and 20% are respectively associated with the Fe oxyhydroxide and the least soluble silicate phases, and <10% to the extraction step where carbonates are assumed to become dissolved. Nickel seems to be the least soluble (Fig. 14A) with >70% extracted by the last extraction step, and >20% is held by the crystalline Fe oxyhydroxides; only <5% of Ni is bound to what is considered to be the carbonate fraction. For Pb (Fig. 14B) the major fraction (70-80%) corresponds to the last extraction step, and only 5-20% of Pb is considered to become easily mobilised, since it is bound to the "carbonate" fraction. Copper is also not easily dissolved (Fig. 14C), since >90% corresponds to extraction

element	Textural class			
	Z and S (sand)	P and L (sandy loam)	A (loam)	G (stony loam); E and U (clay)
As	10	15	20	30
Cd	1	1	1	1
Cr	80	150	200	300
Cu	15	25	25	30
Mn	500	800	800	2000
Ni	10	20	40	80
Pb	50	50	50	50
Zn	100	100	150	200

Table 5. Relation between soil-type and heavy metal and arsenic contents (in mg/kg) according to De Temmerman et al. (1982)

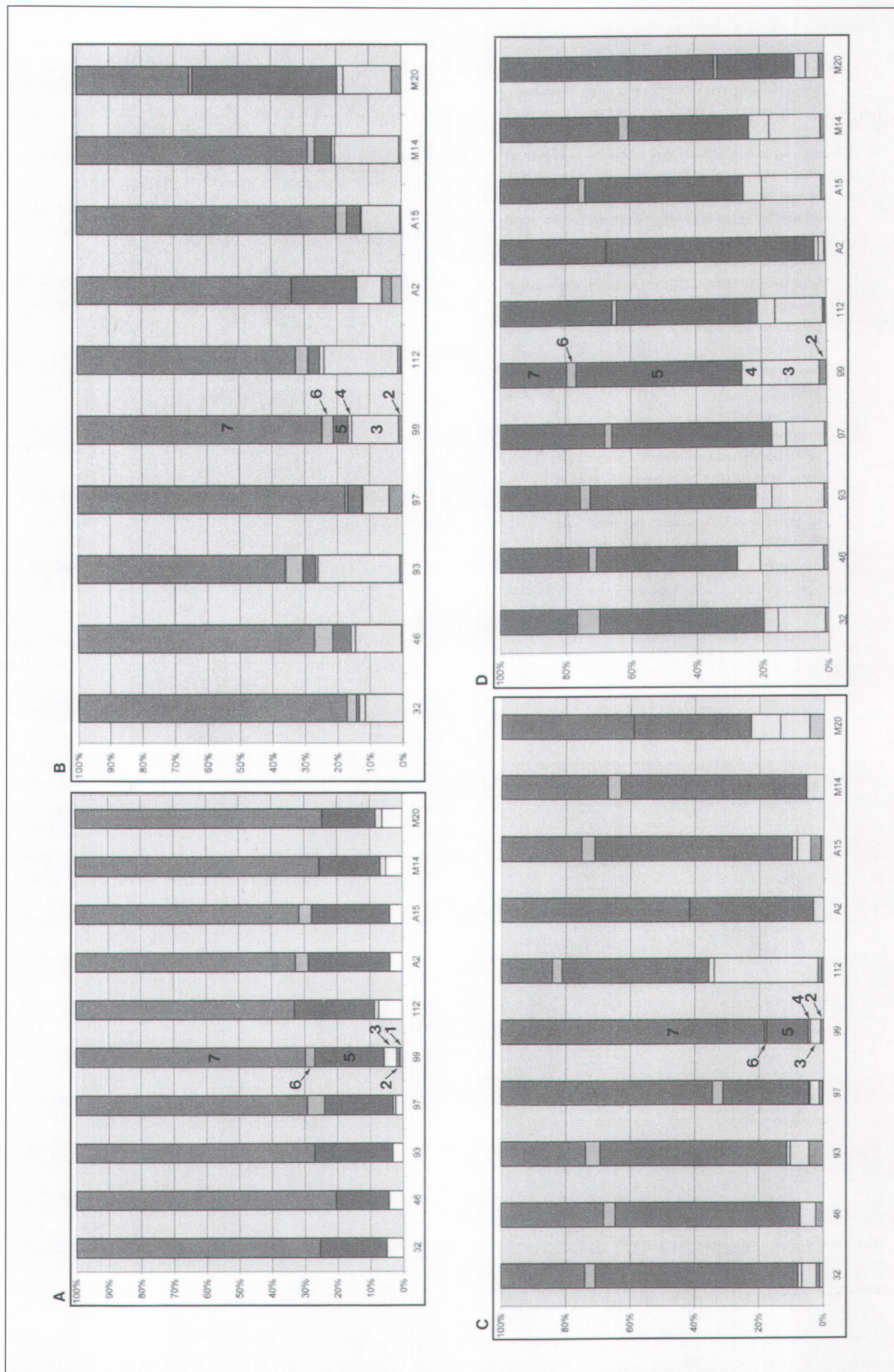


Figure 14. Results of the sequential extraction; A for Ni; B for Pb; C for Cu and D for Zn.

steps (5) and (7), i.e., Fe oxyhydroxide and silicate phases. Zinc shows a similar pattern (Fig. 14D) with >80% extracted by the latter two extraction steps. However, 5-15% of Zn is bound to the "carbonate" phase. Results for Cd clearly show that it is dominantly bound to the "carbonate" fraction. Since most Cd values are close to the detection limit and analytical error is high, results are not discussed further, because their reliability is questioned.

The sequential extraction results reflect the comparatively strong affinity of most heavy metals to be bound to Fe oxyhydroxides and silicates, which are phases that are not easily dissolved under natural oxidising conditions. Therefore, the eco- and human toxicological risk is considered to be minor.

9. Conclusion

This is the first study to present the results of a detailed baseline geochemical mapping project for a number of major and trace elements (i.e., Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn) in a residential area and its rural surroundings in Belgium. As expected the geochemical distribution patterns in agricultural and forested areas reflect mainly natural patterns with minor anthropogenic influences. It is quite apparent that the geological substrate and soil-type exert a major control on element concentrations. Within residential and industrial areas, element patterns reflect to some extent, anthropogenic interferences. This is, for example, the case for Ca and Mg, where anthropogenic activities have an influence on the natural patterns. These influences are also well pronounced in the heavy metal distribution patterns, whereby concentrations 2 to 3 times the natural local background range have been reported. Nevertheless, in general, heavy metal concentrations are below reported intervention values. Based on the results of selective extraction analysis, most heavy metals are strongly bound, indicating that despite the fact that elevated heavy metal concentrations have locally been recorded (e.g., Zn up to 1400 mg/kg, Pb up to 510 mg/kg), the eco- and human toxicological risk is considered to be minor.

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11. References

- AVRIL, A., 1973. Texte explicatif de la planchette de Rochefort 186 W / Verklarende tekst bij het kaartblad Rochefort 186 W. Carte des sols de la Belgique / Bodemkaart van België. IRSIA S. I. 115 pp.
- ALLISON, L.E., 1960. Organic carbon, *In*: C.A. Black et al. (Ed) *Methods of soil analysis*, Part 2. Am. Soc. of Agron., Inc. Madison, Wisc.: 1367-1378.
- BLONDIEAU, M., 1993. Les ressources minerales de la Caestienne et leur exploitation. *In*: De la Meuse à l'Ardenne, n°16, La Caestienne: 35-53.
- Clarit, 1997. <http://www.epa.gov/cgi-bin/claritgw>. Claritweb Image: 600R97115: 7-84.
- DAVY, R., PIRAJNO, F., SANDERS, A.J. AND MORRIS, P.A., 1999. Regolith geochemical mapping as an adjunct to geological mapping and exploration; examples from three contiguous Proterozoic basins in Western Australia. *J. Geochem. Explor.*, 66: 37-53.
- DE TEMMERMAN, L.O., ISTAS, J.R., HOENIG, M., DUPIRE, S., LEDENT, G., VAN ELSEN, Y., BAETEN, H., DE MEYER, A., 1982. Onderzoek naar de 'normale' gehalten aan spoorelementen in een aantal Belgische bodems als basis voor de detektie en het onderzoek van bodemvervuiling. *Landbouwtijdschrift*, 35(2): 1883-1911.
- DE WALQUE, L., BOUCKAERT, J. AND MARTIN, H., 1976. Géochimie de surface et minéralisations du Paléozoïque de Belgique. III. Plomb, zinc et fer au voisinage de l'ancienne exploitation minière de Heuren-Famenne. *Belg. Geol. Survey Professional Paper*, 1976/1, N. 126: 35 p.
- HAWKES, H.E. and WEBB, J.S., 1962. Geochemistry in mineral exploration. *Harper & Row Publishers*, 415 p.
- HERAIL, G., LAGOS, J. AND VIVALLO, W., 1999. Gold dispersion in Andean desert environments (Atacama, Chile). *J. Geochem. Explor.*, 66(3): 427-439.
- KERSTEN, M. AND FÖRSTNER, U., 1986. Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. *Wat. Sci. Technol.*, 18: 121-130.
- KONERT, M. AND VANDENBERGHE, J., 1997. Comparison of laser grain size analysis with pipette and sieve analysis: a solution for the underestimation of the clay fraction. *Sedimentology*, 44: 523-535.

LEVINSON, A.A., 1974. Introduction to Exploration Geochemistry, *Applied Publishing Ltd*; Wilmette, Illinois, 614 pp.

OFFICE WALLON DES DECHETS, 1999. Direction des infrastructures de Gestion des Déchets, 1999. Réhabilitation des dépotoirs et assainissement des sols: le point sur la situation en Région wallonne et ses perspectives d'évolution (version du 14 juin 1999). http://mrw.wallonie.be/dgrne/owd/dossiers/depotoirs_juin99.htm.

OVAM, 1996. Vlaams reglement betreffende de bodemsanering – VLAREBO. Beleidsdokument Sanering. Mechelen, 64 pp.

ROSE, A.W., HAWKES, H.E. AND WEBB, I.S., 1979. Geochemistry in Mineral Exploration. *Academic Press*, London, 657pp.

SCHRAPS, W.G. AND BAUMGARTEN, H., 2000. Investigation and large-scale mapping of soils in urban areas – testsite Krefeld. Conference Proceedings of the seventh International FZK/TNO Conference on Contaminated Soil, "Consoil 2000": 206-213.

SWENNEN, R. AND VIAENE, W., 1981. Litho-geochemistry of some carbonate sections of the Dinantian in the Vesder Region (Belgium). *Bull. Soc. belge Géol.*, 90: 65-80.

THORNTON, 1995. Metals in the Global Environment: Facts and Misconception, International Council on Metals and the Environment, Ottawa, Canada, 103pp.

TUREKIAN, K.K., 1977. Geochemical distribution of elements. In: *Encyclopedia of Science and Technology* (4th ed.). *McGraw-Hill*, New York: 627-630.

TUREKIAN, K.K. AND WEDEPOHL, K.H., 1961. Distribution of the elements in some major units of the earth's crust. *Bull. Geol. Soc. Am.*, 72: 175-192.

VANDENVEN, G., 1973. Coupe géologique de la Tranchée "Distrigaz" – Le tronçon "Hargimont – Nassogne". Synthèse structurale du domaine méridional du Synclinorium de Dinant au méridien "Sinsin-Nassogne". *Belg. Geol. Survey Professional Paper*, 1973/10 N. 93, 24 p.

VAN DER SLUYS, J., BRUSSELMANS, A., DE VOS, W. AND SWENNEN, R., 1997. Regional geochemical maps of overbank and stream sediments in Belgium and Luxembourg. Volume III: Geochemical maps of Belgium and Luxembourg based on overbank and active stream sediments. *Belg. Geol. Survey Professional Paper*, 1997/1, N° 283, 93 p.

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