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# Multi-elemental EDXRF mapping of polluted soil from former horticultural land

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# Abstract

The distribution of major and trace elements was systematically investigated by use of energy dispersive X-ray fluorescence spectrometry (EDXRF) on a former horticultural soil. The purpose of the study was to combine mapping of soil element concentration levels with multivariate statistics for characterisation of soil metal pollution in relation to previous and present land use. A 1-ha study site was chosen from a former horticulture where a previous preliminary survey indicated increased concentration levels of toxic elements. The soil was sampled from the top 20 cm of the soil surface in a  $10 \times 10$ -m grid-like pattern covering the 1-ha study area. In addition, three soil profiles were studied. The elemental composition of the soil samples was investigated by EDXRF while the composition of aqueous soil extracts was determined by total reflection X-ray fluorescence spectrometry (TXRF). Based on mapping and multivariate statistically analysis of the data obtained by EDXRF, most elements were found in almost constant concentration levels in the top soil throughout the investigated site. However, the contents of the toxic elements Zn, Cu, As, and Pb were found to vary significantly within the area. Hence, the samples with high accumulations of As also contained relatively high amounts of Zn, Cu, and Pb, which indicates that toxic-element-containing pesticides have been applied to the soil surface in the area of the former green houses at the study site. The Pb/As mass ratio in the soil indicates that PbHAsO<sub>3</sub> was the preferential lead arsenate used for pest management at the investigated site, while Cu as Bordeaux liquid (CuSO<sub>4</sub>) and Zn were applied to minimize the leaf damaging effect from the former compounds. Calculations indicated that As annually was applied to the soil in the former greenhouses in doses up to 4 kg As/ha while Pb had been annually applied in doses up to 12 kg Pb/ha. The enrichment of Zn, Cu, As and Pb was greatest in the top 20 cm of the soil and no anthropogenic enrichment of these elements occurred below a depth of 50 cm, indicating that the toxic elements are rather immobile in this soil. The results of this investigation suggest that EDXRF used in combination with multivariate statistics is a strong tool for multi-element mapping of elemental contents, sources and mobility in the terrestrial environment.

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# 1. Introduction

Field-based portable and nondestructive rapid XRF techniques, most spectacularly demonstrated during The Mars Pathfinder Mission, have been used for multielemental analysis of soils for environmental characterizations. However, so far the use of XRF-techniques has mainly been limited to screening purposes, because the detection limits are moderate and the precision is not in accordance with the demand for accurate quantitative analysis (Fiorini and Longoni, 1998; Boyle, 1999). Applying a recently developed rapid and versatile laboratory energy dispersive X-ray fluorescence spectrometry (EDXRF) equipment (incl. hardware and software), together with a sample pre-crushing procedure, offers a suitable EDXRF quantification of elements in soil (Laursen et al., 1999,

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2001). This EDXRF method has proven to be efficient, reproducible and accurate for most elements above atomic number 13.

The chosen study area is a part of a former horticulture, established in the 1930s. During this period, a considerable amount of toxic-element-containing pesticides was used worldwide for pest management in horticulture. This use may have caused significant accumulations of toxic elements in the topsoil of former horticultural land. While elevated soil Pb, As, and Cu levels have been reported in orchard soil (Francek, 1997; Aten et al., 1980; Veneman et al., 1983; Peryea and Kammereck, 1997), no published studies relate soil element contents in horticultural soil to the former application of toxic-element-containing pesticides. Horticultural soil has often been intensively used for several years and, hence, high amounts of toxic-element-containing pesticides have been applied. However, as toxic elements and heavy metals have high retention times in soil, elevated concentrations are often found many years after the applications, and have to be assessed in relation to current and future land use. The study site, which today is a recreational area, is on this basis suspected of been polluted with toxic elements that could pose a possible risk to its users.

A detailed multi-elemental mapping of soil elements in 1 ha of the horticultural land has been carried out to investigate how soil elements levels can be related to previous land use. Furthermore, the EDXRF technique has been used in combination with total reflection X-ray spectrometry (TXRF) to study the mobility and fate of toxic elements within polluted and background concentration level soil profiles on the former horticulture. Hence, the purpose of this work is to use the abovementioned EDXRF method in combination with mapping and multivariate statistics to characterise the study area both concerning general soil properties and a possible pollution with toxic elements due to former land use.

#### 2. Experimental section

## 2.1. Study site

Selection of the study site was based on information regarding former horticultural activity in the area. The site is located 20 km west of the centre of Copenhagen in the forest area named "Vestskoven". The size of the study site was 1 ha  $(100 \times 100 \text{ m})$ , and the former horticulture is today used as a recreational oak forest. Aerial photos from 1958 and land registration maps from 1936 reveal that the study site was a horticulture with two greenhouses, established in the year 1934 in the southwestern part of the site (see Fig. 1) while the northern part had been used for outdoor vegetable gardens. The horticulture grew many different vegetables; however, old records indicate that tomatoes, melons and flowers were the main products in the greenhouses. In 1952 the horticulture started a mushroom production in the greenhouses that ended



Fig. 1. Study area. (a) Sampling grid; distance between samples, 10 m. (b) Current land use; the areas are covered with oak trees planted in period 1986 to 1996 and today used for recreational activities. (c) Previous land use during the period 1934 to 1986 where the study area was used for horticultural production. The locations of former green houses, furnace and outdoor vegetable gardens are shown.

in 1986, where all buildings were removed from the area and a public forest was established. Hence, the present oak forest at the study site was planted in the period 1986 to 1996.

Little data could be obtained, either through written records or oral histories, concerning the exact spraying history of the horticulture. However, it is known that spraying with lead arsenate and other toxic-elementcontaining pesticides was likely in the 1930s when the greenhouses at the site were built, and these pesticides were popular and legal to use until the late 1950s. These pesticides were generally applied in high doses and often several times during a growing season due to pest attack.

The soil was formed on clayey till from the Weichselian Glaciation and poorly drained in the southwestern part of the site. Due to the poor draining conditions and hence possible negative effect on root development, the newly planted oak trees were planted in soil banks made of the old A-horizon from the time of the horticulture, thus leaving the B-horizon on top between the tree rows.

# 2.2. Soil and soil profile sampling

The soil was sampled in a  $10 \times 10$ -m grid-like pattern from the soil surface of the 1-ha plot at the former

horticulture, giving a total of 100 samples. The samples were taken as cores with an aluminium cylinder to a depth of 20 cm and sealed into plastic bags until further use. Based on the surface distribution of the soil elements, three soil profiles were established; Fig. 1. One profile was located in a part of the area considered to represent the local background concentration level of the elements (Fig. 1) while the two others were considered to be in contaminated soil areas of the site. According to the Soil Taxonomy system (Soil Survey Staff, 1999), the soil profiles are generally classified as Oxyaquic Argiudol. However, in the upper 30–50 cm of the soil profile at some places within the study area, the soil is seriously affected by demolition waste disposal from the buildings previously located at the site.

# 2.3. Sample preparation and analysis

The samples were air-dried, homogenized and sieved through a stainless steel 2-mm screen for further characterization. While pH was determined in all soil samples, the general soil parameters texture, CEC<sub>7</sub>, organic and inorganic carbon were analysed on a subset of 23 soil samples from the profiles (Soil Science Society of America Book Series, 1996).

Total elemental concentrations in surface samples and samples from soil horizons were measured by EDXRF. Generally, sample preparation and EDXRF analysis followed the description by Laursen et al. (1999, 2001). However, the sample preparation was slightly modified compared to the description of Laursen et al. (2001): Samples of 5 g were grounded with 7 ml of water in a McCrone Micronizer Mill at 1400 rpm for 20 min producing a suspension of particles with a size smaller than 2 µm. This soil suspension was diluted with triple ion exchanged water to a suspension concentration of 2500 mg particles/dm<sup>3</sup>. One milliliter of the soil suspension was applied to a polypropylene film with a cationic detergent (hexadecylmethylammoniachlorid) to obtain an air-dried homogeneous thin sample layer. Dependent on the soil CEC<sub>7</sub>, the detergent was added to the suspension in the concentration range of  $10^{-6}$  to  $10^{-4}$  M. As the soil CEC<sub>7</sub> was found to correlate well with a logarithmically quantified measure of the soil color, as determined by Munsell® soil color charts, the accurate amount of detergent applied to the suspension was determined by use of the Munsell® soil color charts (Munsell Soil Color Charts, 2000).

The EDXRF spectrometer consisted of a Philips compact X-ray generator (PW 1830/40) with a table-top 3-kW Mo anode diffraction tube (PW2275/20) mounted on a (PW1831/00) cabin together with a Kevex Superdry 20 mm<sup>2</sup> Si(Li) detector. A highly oriented pyrolytic graphite (HOPG) crystal served as monochromator for the incident tube radiation resulting in a monoenergetic excitation source (the characteristic 17.44 keV Mo K $\alpha$ 

line). For data processing, a Kevex (4561A) pulse processor connected to a PC-based ADC and data acquisition card (Nucleus PCA3) was used, while the software program X-Spec32 had recently been developed for routine quantitative major, minor, and trace element analysis of the dried thin film soil samples (Laursen et al., 1999, 2001).

Two NIST standard reference soil materials, NIST SRM 2709 and NIST SRM 2711, from National Institute of Standards and Technology (National Institute of Standards and Technology, 1993) were analysed under similar conditions as the samples. All laboratory equipment used was soaked and rinsed in 6.5% nitric acid (analytical grade) for a minimum of 60 min with exception of the milling vials and pieces for the McCrone Micronizer Mill, which were rinsed three times with triple ion exchanged water followed by three times 1% nitric acid solution and finally three times triple ion exchanged water. This washing procedure of the milling vials and pieces minimized the washing time and thereby the sample preparation time.

Soil solutions in the soil profile were simulated by use of standardised aqueous extraction on the soil samples collected in intervals of 10 cm down the three soil profiles with subsequent determination of the elemental composition of the soil extract by total reflection X-ray fluorescence spectrometry (TXRF). The aqueous extraction was performed by use of triple ion exchanged water with a liquid to solid ratio (L/S) of 2 l/kg (European Committee for Standardisation, 2002). Gallium was added to the soil solution extract as internal standard in a total concentration of 0.4 mg Ga/l and the soil solution extract was placed on a Si-plate and measured by TXRF. The TXRF method is described elsewhere (Moloi et al., 2002). The instrument used consists of a Siemens 18-kW rotating anode with a Mo-target (focus size 0.5×10 mm, specific load 3.6 kW/ mm<sup>2</sup> with a Kevex Si(Li) 80 mm<sup>2</sup> detector; Pettersson and Boman, 1996).

# 2.4. Statistical data evaluation

All soil sample data were evaluated by a principal component analysis (PCA) in the chemometric data programme "The Unscrambler 6.2" (Esbensen, 2000). Here each observation is presented geometrically as a point in a k-dimensional space with the variables as k-coordination axes. The elemental concentrations could differ by more than six orders of magnitude, and some data often had incompatible unites, which were eliminated by data normalisation, making no single element more important than another. All normalised variables were scaled to equal deviation (auto-scaled) before calculation and the data were centred. Non-detectable element concentrations were treated as missing values.

The PCA has in this study been used to find elements which exhibit a large variation compared to other

elements (P=0.95). Furthermore, the PCA was used to find elements showing high correlation coefficients (Covariation) which have been interpreted as elements with same origin, e.g., natural or anthropogenic.

A total of three successive PCAs were accomplished:

- The principal component analysis (PCA) was applied to all the elemental concentration data of the top soil, constituting a matrix of 25 (variables, elemental composition)×99 (samples). This matrix describes the overall elemental variation at the study site. One outlier was detected in the data set. The classification of the sample as outlier in the PCA was based on its minor influence on the residual sample variance (3%) but its high influence on the leverage (>1) in the data set. Further, the outlier sample consisted of a diverging material (building sand) compared to the remaining 99 samples. The outliner sample was excluded from the data set, as it was not representative for the study area. A PCA was carried out for the elemental concentrations measured in the soil matrix of the three soil profiles at the study area. In this PCA the matrix constituted of 25 (variables, total elemental concentrations in the soil samples)×23 (samples); data are not shown.
- A PCA was carried out on element concentrations from the simulated soil solution of the 3 soil profiles. The PCA matrix constituted of 17 variables (elemental concentrations in simulated soil solutions) and 23 samples. The results of this PCA are not shown.

#### 3. Results and discussion

The elements are grouped in major elements and trace elements, separated at a mass concentration of 100 mg/kg soil. Furthermore, the trace elements are arranged into two groups: (i) Toxic elements with a relatively well-known environmental impact, i.e., Cr, Co, Ni, Cu, Zn, As, and Pb; and (ii) elements with less environmental impact or elements where only limited information regarding occurrence and fate in the soil environment is available.

# 3.1. Accuracy and precision of the EDXRF method

The accuracy of the EDXRF method was documented by the analysis of two certified soil reference materials (NIST SRM 2709 and NIST SRM 2711) (National Institute of Standards and Technology, 1993). Typically, the average accuracy of the determinations is better than  $\pm 20\%$  of the certified values; see Table 1. Deviations from this are primarily related to poor sensitivity for fluorescence or a lower concentration range for certain elements, i.e., Mg, Al, and Th (data not shown). Other deviations may be related to difficulties with determination of the net peak area due to peak overlap among elements like As and Pb, Fe and Co, Ti and Ba, and V and Cr. Hence, a high Pb concentration can affect the concentration of As and vice versa. However, it is possible for the EDXRF instrument to determine the concentrations of these elements accurately, when they occur in low to moderate concentrations in soil.

Table 1

Element concentrations measured in the soil reference material NIST SRM 2709 and NIST SRM 2711 from National Institute of Standards and Technology

Element	Total content (mg/kg)				
	NIST SRM 2709		NIST SRM 2711		
	EDXRF measured	Certified value <sup>a</sup>	EDXRF measured	Certified value <sup>a</sup>	
Si	30.9±0.2 (wt.%)	29.7±0.2 (wt.%)	30.0±0.3 (wt.%)	30.4±0.2 (wt.%)	
K	1.91±0.05 (wt.%)	2.03±0.06 (wt.%)	2.37±0.05 (wt.%)	2.45±0.08 (wt.%)	
Ca	1.40±0.09 (wt.%)	1.89±0.07 (wt.%)	2.58±0.06 (wt.%)	2.88±0.08 (wt.%)	
Ti	0.36±0.01 (wt.%)	0.34±0.02 (wt.%)	0.29±0.02 (wt.%)	0.31±0.02 (wt.%)	
V	$163 \pm 10$	$112\pm 5$	97±3	81.6±3	
Cr	$131 \pm 31$	$130 \pm 4$	97±3	(47)	
Mn	$667 \pm 44$	$538 \pm 17$	814±3	$638 \pm 28$	
Fe	4.02±0.27 (wt.%)	3.50±0.11 (wt.%)	2.94±0.08 (wt.%)	2.89±0.06 (wt.%)	
Со	$14.9 \pm 0.1$	$13.4 \pm 0.7$	$18.2 \pm 1.2$	(10)	
Ni	82.1±6.9	88±5	$26.3 \pm 3.7$	$20.6 \pm 1.1$	
Cu	$64.7 \pm 0.8$	$34.6 \pm 0.7$	124±9	$114\pm 2$	
Zn	126±8	$106 \pm 3$	$374 \pm 15$	$350\pm 5$	
As	24.2±5.1	$17.7 \pm 0.8$	279±9	$105 \pm 8$	
Ga	$18.1 \pm 1.7$	(14)	$38.5 \pm 0.7$	(15)	
Rb	$104 \pm 6$	(96)	$128\pm 5$	(110)	
Sr	$209 \pm 11$	$231 \pm 2$	$229 \pm 22$	$245 \pm 1$	
Υ	$17.7 \pm 0.5$	(18)	nd. <sup>b</sup>	(25)	
Ba	$674 \pm 50$	$968 \pm 40$	$671 \pm 9$	$726 \pm 38$	
Pb	$22.0 \pm 0.4$	$18.9 \pm 0.5$	851±17	$1162 \pm 31$	

<sup>a</sup> Uncertified values are shown in brackets.

<sup>b</sup> nd. means non-detectable.

The precision of the method was generally better than 10%, determined as the relative standard deviation of the determination of eight subsamples of one soil sample. The only elements exceeding a standard deviation of 10% were V (19%), Cr (15%), Ni (21%) and Th (23%).

Based on these results, the employed EDXRF method demonstrates both adequate accuracy and precision for determining the variation in elemental concentrations at the study site. However, when large amounts of As or Pb are present as one of the certified reference materials (Table 1), analytical deconvolution problems may diminish the precision of the exact concentration values.

# 3.2. Soil properties and elemental concentrations

The soil profiles are classified as Oxyaquic Argiudol according to the USDA soil classification system (Soil Survey Staff, 1999). The pH of the top-soil (pH  $\approx$  7) is somewhat higher than that of typical forest soils, which is a result of liming at the former horticulture. The soil has not been limed since the forest was established in the period 1986 to 1996, but lime fragments were still evident in the top 20 cm of the soil profiles. Anthropogenic influences were present in most soil samples in the form of coal cinders, fragments of glass, and rubble in the top 20 cm of the soil. Furthermore, the foundation of a former building was discovered in one of the three soil profiles.

The ranges of the elemental concentration in the soil samples are presented in Table 2, in addition to the mean

Table 2

Minimum, maximum, and average concentrations of the measured elemen	its
compared with average background concentration levels	

Element	Concentrations (mg/kg)			
	Measured range	Measured, average±std	Background level, average±std <sup>a</sup>	
Si	76.9-89.6 (wt.%)	81.9±1.5 (wt.%)	81.8±0.74 (wt.%)	
Κ	1.03-1.80 (wt.%)	1.54±0.09 (wt.%)	1.56±0.06 (wt.%)	
Ca	0.26-2.7 (wt.%)	1.02±0.52 (wt.%)	0.84±0.33 (wt.%)	
Ti	0.04-0.25 (wt.%)	0.21±0.02 (wt.%)	0.22±0.01 (wt.%)	
V	27-100	$75 \pm 15$	$73 \pm 15$	
Cr	7.5-78	$51 \pm 10$	$50 \pm 9.4$	
Mn	62-649	$308 \pm 67$	$307 \pm 61$	
Fe	0.17-1.9 (wt.%)	1.33±0.19 (wt.%)	1.37±0.10 (wt.%)	
Co	5.6-98	$69 \pm 11$	$71 \pm 7.4$	
Ni	4.4–28	$9.3 \pm 3.3$	$7.8 \pm 1.1$	
Cu	13-269	$42 \pm 37$	$27 \pm 3.3$	
Zn	16-247	$107 \pm 49$	$79 \pm 9.8$	
Ga	2.8-11	$8.3 \pm 1.2$	$8.7 \pm 0.88$	
As	3.9-39	$11 \pm 6.3$	$8.7 \pm 1.6$	
Br	2.4-16	$6.0 \pm 2.4$	$5.9 \pm 1.6$	
Rb	36–94	$71 \pm 7.6$	$72 \pm 5.2$	
Sr	63-131	97±12	$96 \pm 8.6$	
Y	2.5-17	$13 \pm 1.9$	$13 \pm 1.3$	
Ва	128-369	$240 \pm 39$	$230 \pm 41$	
Pb	17-157	$36 \pm 23$	$23 \pm 3.2$	

<sup>a</sup> Mean local background concentration level has been determined as average concentrations of 20 soil samples collected in the northern part of the sampling area. local background concentration levels of the elements. Most major and trace elements determined show only limited variation in concentrations at the study site. Thus, it is likely that the major and trace elements revealing little variation at the study site are of natural origin. The concentrations of the elements Ca, Cu, Zn, As and Pb varied substantially, most likely due to the previous land use. Table 2 shows the minimum and maximum concentrations determined. The very low minimum concentrations for all elements except Si come from one particular sample (classified as outlier in the PCA below) of construction sand and the minimummaximum range is therefore not representative for the study area.

Generally, the determined elemental concentration levels are greater than published background values for similar geological material; see, e.g., Tjell and Hovmand (1978). This difference most likely reflects the fact that EDXRF determines the total amounts of elements in the soil, whereas published results most often represent the nitricacid-digestible part of the soil that does not include the elemental content in the silicate matrix part of the soil material. However, the average concentrations of Cu, Zn, As and Pb in this study are up to several orders of magnitude larger than the published values for toxic elements in similar soils, which strongly indicates that parts of the study area have been enriched with these elements.

The concentrations of toxic elements determined in this study are moderate compared to levels found on orchard surfaces soil worldwide. Aoyama and Kuroyanagi (1996) reported concentrations of up to 166 mg/kg As in an apple orchards in Japan, while Merry et al. (1986) found concentrations of 140 mg/kg As. Likewise the concentrations of Pb are generally much higher in orchard studies than in this horticulture. However, only few studies relate the Cu and Zn content in orchard soil to the previous use of toxic-element-containing pesticides, and it is therefore difficult to compare measured concentrations of these elements with literature values.

# 3.3. Soil surface distribution of elemental concentrations

Based on the analysis of 20 soil samples from the northern part of the study site (Fig. 1), a local background elemental concentration level was defined. These soil samples were chosen as reference data set for background levels because no previous use of toxic-element-containing pesticides was expected in this area. Comparisons between the element concentrations (Table 2) in the local background samples and the other samples show that samples from the southwestern part of the study site (Fig. 1) contained up to five times higher elemental concentrations relative to the background level. In particular, the concentrations of Pb and As exceeded by far the current standards for clean soil of 40 mg Pb/kg and 20 mg As/kg, respectively.

In order to explain the variance in the data shown in Table 2, the results of the PCA carried out on element



Fig. 2. (a) Score plot and (b) loading plot for the principal component analysis of top soil samples from Vestskoven, Denmark. The score plot shows the distribution of the samples according to PC1 and PC2. The loading plot (b) shows the contribution of the variables to PC1 and PC2. Ninety-nine soil samples and 25 variables are used in the calculation.

concentrations in the topsoil samples are shown in Fig. 2. Fig. 2 shows a score plot and a loading plot of PC1 and PC2 representing the largest sample residual variance (PC1) and the second largest sample residual variance (PC2). PC1 (Fig. 2) represents 49% of the sample residual variance in the data set and is related to the concentration of Mn, Zn, As and Pb. PC2 represents 28% of the sample residual variance, and, according to Fig. 2, the variation in concentrations of Cu is responsible for PC2. Variations in the Ba concentration are responsible for PC3 (11%), while variations in the Ca concentration are responsible for 6% of the sample residual variance (PC4) of the samples (data not shown).

The loading plot in Fig. 2 shows a close relation between the concentrations of the elements Mn, Zn, As and Pb (covariation). Thus, a high concentration of As is expected to be associated with high concentrations of Mn, Pb and Zn. When analysing the score plot in Fig. 2, it is found that the variation of Zn, As and Pb concentrations is very systematic, with high concentrations of these elements in a specific area of the study site compared to samples centred around the middle of the score plot representing the remaining study site. The likely conclusion is therefore that As, Pb, and Zn have been applied to this specific area of the study site as the soil type and content of major elements in this area do not differ from the other samples.

As mentioned above, Mn is also a contributing factor to PC1; however, as can be seen in Fig. 2, particularly one sample has a high content of Mn, which makes this element a significant contributor to PC1. If the PCA in Fig. 2 is recalculated without this sample, Mn no longer contributes significantly to PC1 and the significance of Mn is not further discussed. The samples contributing to PC2 can be found in the score plot in Fig. 2 where mainly four samples

contribute to PC2. These four samples all have a high content of Cu compared to the average sample. However, the samples do not differ in texture or content of major elements. It is therefore likely that the greater Cu concentrations are connected to anthropogenic use of the soil. In the loading plot in Fig. 2, it can also be seen that there is a general connection between Cu and Zn, As and Pb as many of the samples contributing to PC1 also have a high Cu content. This result indicate that there can be a connection between Cu and Zn, As and Pb in a particular area of the study site.

As mentioned above, the third PC is explained by variance in the Ba concentrations in the topsoil samples. According to the score plots of PC3 (not shown), this variation is mainly due to a very high concentration of Ba in one sample and, hence, as for Mn the influence of this single differing sample with respect to the content of Ba is not further discussed.

Variations in the Ca concentration, according to the PCA, account for 6% of the residual variance in the samples. This result is most likely due to different liming conditions at the site as the study area has been limed in different stages, due to forestation in 1986, 1992 and 1996. Hence, the samples from the area planted in 1996 contain slightly higher Ca concentrations than the samples from the areas planted in 1986.

The distribution of the determined total soil concentrations of Cu, Zn, As and Pb is presented in Fig. 3, which allows for comparison with the previous land uses. Systematically elevated concentrations of Zn, As, Pb and Cu are seen in the southwestern part of the study site (Fig. 3). In the eastern part of the study area (Fig. 3a and d), where a coal furnace was located, it is possible to identify hot spot concentrations of Cu and Zn. The influence of coal incineration and ash production cannot be assessed directly. Most soil samples contained cinders, and the furnace activity may have affected the total content of Cu and Zn in the soil samples; confer e.g., van der Sloot et al. (1996). At several data points of the southwestern part of the area, it is observed (Fig. 3a-d) that the concentrations of Cu, Zn, As, and Pb are much greater (>200%) in this area than the local background concentration level (Table 2). Greenhouses have previously covered this area (see Fig. 1) and it seems therefore likely to relate the general accumulation of toxic elements in this area to the previous use of toxicelement-containing pesticides in the greenhouses. A 200% enlargement of As and Pb compared to the background level corresponds to an accumulated enrichment of 6.5 g  $As/m^2$ and 19.5 g Pb/m<sup>2</sup> in the area of the previously located greenhouses. These results correspond to an annual application rate of 4 kg As/ha and 12 kg Pb/ha in the period 1936 to 1950.

According to relevant spraying manuals from the late 1930s, the application of lead arsenate in doses between 2 and 2.5 kg/ha per treatment was recommended for pest management of crops like tomatoes, melons and flowers. Furthermore, the greenhouses were generally treated with lead arsenate twice a year. However, the application rate of lead arsenate seems rather moderate compared to similar investigations in apple orchards. Examination of the lead arsenate used in New Jersey, USA reveals that orchards were applied lead arsenate in doses between 12 and 50 kg/ ha annually (Murphy and Aucott, 1998).

The accumulated lead and arsenate exceed the current human health soil quality criteria mentioned above and the investigated horticulture only existed during a short part





Fig. 3. Surface distribution of (a) zinc, (b) arsenic, (c) lead, and (d) copper at the investigated area in Vestskoven, Denmark.

of the period where toxic-element-containing pesticides were used. Hence, other horticultures could be facing more serious problems coursing limitation in land use due to previous long-term use of toxic-element-containing pesticides.

The distribution of As throughout the area of the former greenhouses followed mainly the same surface pattern as Pb. This indicates further that Pb and As have been applied together, presumably as lead arsenate. No reliable information about the type of pesticide employed in this particular previous horticulture is available. However, according to Veneman et al. (1983), it is possible to determine the compound(s) applied by use of the Pb/As mass ratio. Hence, orthoarsenate (Pb<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>) has a Pb/As ratio of 4.14, while acid orthoarsenate (PbHAsO<sub>3</sub>) has a Pb/As mass ratio of 2.77 and basic orthoarsenate (Pb<sub>4</sub>(PbOH)(AsO<sub>4</sub>)<sub>3</sub>) a mass ratio of 4.62 (Veneman et al., 1983). In order to investigate the type of lead arsenate used, the mass ratio of Pb/As in the top soil was determined. The mass ratio (Pb/As) calculated by linear regression of the surface data gave a value of 2.84  $(Y=2.84X+4.32, R^2=0.62)$ , indicating that the preferential lead arsenate used was PbHAsO3. This estimate is uncertain, as deconvolution occurs between the As and Pb peaks where large concentrations of As and/or Pb are present. However, as the concentrations of Pb and As in this study are closer to the concentration range in NIST Standard 2709 than in NIST Standard 2711 (Table 1), it is likely that the deconvolutions of As and Pb peak areas are too small to affect the measurements of As and Pb concentrations profoundly.

According to Veneman et al. (1983), the slightly higher Pb/As ratio found in this study might be the result of a very slow dissolution of the lead arsenate leading to some leaching of As. However, another explanation could be that the mass ratio of lead arsenate varies a little due to gardener-mixed compounds, which may differ from prefabricated mixtures following the theoretical ratios.



Fig. 4. Zinc, Arsenic, Lead total soil concentrations in a contaminated soil profile from the sampling area in Vestskoven, Denmark.



Fig. 5. Zinc, Arsenic, Lead total soil solution concentrations in a contaminated soil profile from the sampling area in Vestskoven, Denmark.

### 3.4. Cu, Zn, As and Pb distribution in soil profiles

The concentrations of Zn, As, and Pb in one of the three investigated soil and soil water profiles are illustrated in Figs. 4 and 5. Zn, As, and Pb accumulate in the upper part of the soil with a maximum concentration in the top 5 cm (Fig. 4). The accumulation of these toxic elements indicates that these are surface-applied and even 50 years after the last toxic-element-containing pesticide application, no significant leaching of the residues has occurred below 50 cm. The Pb/As ratio mentioned above is fairly constant in the top 20 cm, indicating that As and Pb still occur as lead arsenate in the soil. Similar results were found by Veneman et al. (1983) and Folkes et al. (2001) indicating that the toxic elements are rather immobile in the soil. Furthermore, this ageing of the lead arsenate in the soil could reduce the toxicity of the soil, because the toxic elements are incorporated in the soil matrix.

While Cu (not shown) is mainly accumulated in the top 20 cm of the soil profile profoundly bound to the organic matter, some redistribution of Zn, As, and Pb has taken place in the upper part of the profile, as an accumulation of these elements is evident at 40 cm. According to the PCA of the elemental composition of the profiles, this redistribution is due to textural changes in the soil as Zn, As and Pb covariate with Al and Fe in the upper part of the profiles. Hence, the toxic element distribution is similar to the distribution of Al and in particular Fe in the profile, indicating that a part of the toxic elements are tightly bound to the clay and Al–Fe oxide minerals. Below 50 cm, no toxic elemental enrichment occurs, and the concentrations in the parent material.

In Fig. 4, the secondary accumulation of Pb and Zn in the soil seems to be due to a slight raise in soil pH from 0 to 30 cm, leading to increased soil particle attenuation at this depth. Hence, the observed distribution coefficient  $K_d$  between the soil and the soil solution water extracts at 30 cm (Pb  $K_d$ =2800 l/kg) is clearly higher than the  $K_d$ 's at 20 and 40 cm. An accumulation of Ca, Sr, Y, and Th takes

place at the same depth, which indicates stronger affinity for the soil phase due to a raise in soil pH.

The distribution of Zn, As, and Pb concentrations in the soil solution extracts is shown for one of the profiles in Fig. 5. The maximum concentrations of Cu, Zn, As, and Pb in the soil solution extract of the contaminated soil profile are: 0.14, 0.29, 0.19 and 0.04 mg/l, respectively. As expected, these values are low due to the adsorption and precipitation processes controlling the solute concentration of the elements. Hence, only 0.07% of the total lead content is available in the soil solution extract while 0.02% Cu, 0.15% Zn, and 0.5% As are represented in the soil solution extract. The results are in accordance with Ng et al. (1998) who found that only 0.6% of As was soluble in the soil solution of a soil profile with a contamination of 1000 mg/kg As. The results indicate that the elements Cu, Zn, As, and Pb are very immobile in the soil, even though high total concentrations of these elements are present. However, a redistribution of the heavy-metal-containing pesticide residues had occurred during the last 50 years probably due to facilitated transport by organic acids or colloidal transport.

Water saturated and reducible conditions are dominant from 70- to 90-cm depth and below in the soil profile (Fig. 5). Generally, the reduced As species As(III) is more soluble and hence more mobile than the more oxidized form As(V) in the soil solution. It is therefore possible that the surface-applied arsenate over time would leach to this depth and change form to arsenic, hence becoming more mobile than in the top soil. Furthermore, water saturated conditions were observed in several places at the study site, particularly in the area of the former greenhouses where high concentrations of As have been found.

#### 3.5. General evaluation and perspectives

Use of the EDXRF method for multi-elemental mapping of toxic-element-containing pesticides in soil has proven to be useful, as the method is relatively simple and inexpensive compared to the size of the data set and number of elements determined. Most of the elements were determined with a satisfactory precision and accuracy.

The distribution of some elements (Ca, Zn, Cu, As, and Pb) varied considerably over the 1-ha study area (relative standard deviation larger than 30%). The elements were accumulated in the upper 20 cm of the soil profile due to the retention by sorption and precipitation processes in the soil. The distribution can be attributed to the use of pesticides in the period from 1880 to 1950. Metals being applied to the terrestrial environment have very long retention times and can still be found many years after their application. Afforestation of the former horticulture land will gradually lead to decreasing soil pH and thereby enhance the mobility of the toxic elements in the soil profile.

The area of distribution of similar sites moderately polluted by previous use of toxic-element-containing pesticides is unknown. However, it is likely that land located close to cities, which previously has been used as horticultures to provide fresh fruit and vegetables to the inhabitants, has either vanished due to the urbanising of the areas or the land use has changed to recreational areas. These changes can affect the bioavailability and mobility of the toxic elements in polluted areas and thereby limit the future soil function and land use.

#### References

- Aoyama M, Kuroyanagi S. Effects of heavy metal accumulation associated with pesticide application on the decomposition of cellulose and orchard grass in soils. Soil Sci Plant Nutr 1996;42: 121–131.
- Aten CF, Bourke JB, Martini JH, Walton JC. Arsenic and lead in an orchard environment. Bull Environ Contam Toxicol 1980;24:108–15.
- Boyle JF. Isotope-source, energy-dispersive XRF analysis of geological materials using gas-filled proportional counters: signal deconvolution using simulated peak shapes. X-Ray Spectrom 1999;28:178–82.
- European Committee for Standardization. Characterisation of waste Leaching Compliance test for leaching of granular waste materials and sludges—Part 1: One stage batch test at a liquid to solid ratio of 2 l/kg with high solid content and with particle size below 4 mm (without or with size reduction). EN 12457-1; 2002.
- Esbensen K. Multivariate analysis in practice A training package for the program "The Unscrambler". Norway: Camo; 2000.
- Fiorini C, Longoni A. Application of a new noncryogenic X-ray detector in portable instruments for archaemetric analyses. Rev Sci Instrum 1998;69:1523–8.
- Folkes DJ, Kuehster TE, Litle RA. Contribution of pesticides use to urban background concentrations of arsenic in Denver Colorado, USA. Environ Forensics 2001;2:127–39.
- Francek MA. Soil lead levels in orchards and roadsides of mission peninsula Michigan. Water Air Soil Pollut 1997;94:373-84.
- Laursen J, Stikans M, Karlsen K, Pind N. A versatile and easy to handle EDXRF instrumentation. In: Fernández JE, Tartari A, editors. Book of proceedings of European conference on energy dispersive X-ray spectrometry. Bologna: Editrice Compositori; 1999. p. 139–44.
- Laursen J, Vestergaard BT, Pind N, Karlsen K, Bruun Hansen HC. Rapid method for EDXRF analysis of clayey and sandy soil. X-Ray Spectrom 2001;30:186–9.
- Merry RH, Tiller KG, Alston AM. The effects of contamination of soil with copper, lead and arsenic on the growth and composition of plants. Plant Soil 1986;91:115–28.
- Moloi K, Viksna A, Lindgren ES, Standzenieks P. Sequential leaching of trace elements in fine-particle aerosol samples on Teflon filters. X-Ray Spectrom 2002;31:27–34.
- Munsell Soil Color Charts. Munsell Color. New Windsor, NY: Gretag-Macbeth; 2000.
- Murphy EA, Aucott M. An assessment of the amounts of arsenical pesticides used historically in a geographical area. Sci Total Environ 1998;218;89–101.
- National Institute of Standards and Technology. Certificate of analysis– Standard reference material 2711 and 2709. USA: National Institute of Standards and Technology; 1993.
- Ng JC, Kratzmann SM, Qi L, Crawley H, Chriswell B, Moore MR. Speciation and absolute bioavailability: risk assessment of arseniccontamination sites in a residential suburb in Canberra. Analyst 1998;123:889–92.

- Peryea FJ, Kammereck R. Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. Water Air Soil Pollut 1997;93:243–54.
- Pettersson RP, Boman J. A total-reflection X-ray fluorescence spectrometer using rotating anode. Nucl Instrum Methods Phys Res, Sect A 1996;371:553–9.
- Soil Science Society of America Book Series. Methods of soil analysis, Part 3 Chemical methods. In: Sparks, D. et al. editor, Soil Science Society of America Inc. American Society of Agronomy, Madison, WI; 1996.
- Soil Survey Staff J. Keys to soil taxonomy; United States Department of Agriculture, Soil Conservation Service. 8th ed. Blackburg: Pocahontas Press; 1999.
- Tjell JC, Hovmand MF. Metal Concentrations in Danish Arable Soils. Acta Agric Scand 1978;28:81–9.
- van der Sloot HA, Comans RNJ, Hjelmar O. Similarities in the leaching behaviour of trace contaminants from waste, stabilized waste, construction materials and soils. Sci Total Environ 1996;178:111-126.
- Veneman PLM, Murray JR, Baker JH. Spatial Distribution of pesticides residues in a former apple orchard. J Environ Qual 1983;12:101–4.