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Lead isotope ratios in a soil from a coal carbonization plant

Mercedes Díaz-Somoano, Montserrat Calvo, M. Antonia López Antón, Isabel Suarez-Ruiz, Roberto García, Sabino R. Moinelo, M. Rosa Martínez-Tarazona *

Instituto Nacional del Carbón (CSIC), C/Francisco Pintado Fe, No. 26, 33011 Oviedo, Spain

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Abstract

In the present work, lead isotope ratios were used to ascertain the enhancement of lead concentration in a soil derived from an experimental coking plant that processed 30 tons of coal per day over a period of 30 years. Isotope ratios were also used in this work to evaluate whether lead originated by this industrial activity may be leached and transported deep into the soil. It was found that variation in Pb concentrations in soil samples from the A Horizon, at various distances (7–35 m) from the coking battery, ranged between 17 and 349 μg g^{-1}, whereas in samples taken 50 m away, the concentration was less than 34 μg g^{-1}. This implies that all the operations involved in coal carbonization are responsible for the increase in the total amount of Pb in the thin top layer of the soil, although the concentration of lead was lower than the intervention limit values established for contaminated soils by Dutch Standards (530 μg g^{-1}). To establish the origin of pollution in this soil, lead isotope ratios of samples taken at different points were determined. The relationships between ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb indicated a mixture of natural and anthropogenic Pb. Although lead from industrial activity is present in the thin top layer, its presence decreased drastically between 0 and 30 cm depth.

Keywords: Lead isotope ratio; Soil; Coal carbonization plant

1. Introduction

Lead is a highly toxic metal that is present in soils in concentrations generally lower than 100 μg g^{-1} [1], but can be as high as 300 μg g^{-1} in agricultural soils [2]. Lead concentrations in coal are generally lower than 80 μg g^{-1} [1]. The established values for lead concentrations according to the Dutch Standards [3] in soils and sediments are 85 μg g^{-1} (target value) and 530 μg g^{-1} (intervention value). Coal carbonization plants are a source of lead and other toxic pollution that may affect the environment, and although some aspects of the impact of this industrial process on the surrounding soil have been evaluated [4,5], the contribution of coke production to the enhancement of trace elements has so far received little attention.

During the coke making process emissions occur in all the operations involved (coal handling, charging, carbonization, coke pushing, coke quenching, coke handling, battery under firing and gas cleaning and by-product plant operations). The sources of pollution may be broadly classified as continuous that are those emitted over the entire carbonization cycle and fugitive or related to specific operations such as charging, pushing, leakages, etc. In the case of continuous emissions, the main pollutants consist predominantly of sulphur, nitrogen oxides and particulates. Fugitive emissions can also involve PAHs, heavy metals, particulates, volatile organic compounds (VOCs) and hydrogen sulphide. All these contaminants are emitted into the atmosphere and, by means of dry and wet deposition, constitute the main input to soil contamination in the vicinity of coking plants. Quenching and pushing have been identified as the sources of highest emission of volatile trace elements from coke works probably due to an enrichment of the emitted dust compared to the feed coal [6].

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* Corresponding author. Tel.: +34 985 119090; fax: +34 985 297662.
E-mail address: rmtarazona@incar.csic.es (M. Rosa Martínez-Tarazona).

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Natural lead is normally composed of four stable isotopes of masses 204, 206, 207 and 208. Among these isotopes only ^{204}Pb is completely non-radiogenic, whereas ^{206}Pb, ^{207}Pb and ^{208}Pb are daughter products from the radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. The Pb isotope ratios depend on how long Pb and its parents were together before the Pb was segregated into the mineral under study [7]. Lead isotope ratios could be used to differentiate local natural lead from external sources of lead contamination, which vary depending on the anthropogenic activity in the area. In fact, stable Pb isotopic ratios, in combination with concentration data for Pb, are a useful method for differentiating natural from anthropogenic lead and discovering sources of Pb contamination [8–12]. Data on lead isotope ratios for different ores and pollution sources, including some coals, are already available in the literature [7,11–17], and may be used for comparing isotope ratios in possible contaminated sites.

Inductively coupled plasma mass spectrometry (ICP-MS) has become the most widely used technique for isotope ratio measurements in a number of applications because it is easy to operate and has a high sample throughput. Furthermore it is a widely available and relatively low cost technique. Although limited precision is obtained by a single collector equipment compared to a multi-collector instrument or a thermal ionization mass spectrometer (TIMS), with a single collector equipment it is possible to screen the isotopic composition and the multielement trace composition very quickly [18].

In the present work, an evaluation of the level of lead contamination and possible sources of pollution in the soil around a semi industrial coking plant that was only used for research in an area free of other sources of industrial contamination that was in operation for 30 years was carried out. In order to evaluate the contribution of the coking activity carried out over several years to soil pollution and to estimate the contribution of coal to the quantity of lead mobilized through the soil profile, lead isotope ratios were determined in soil samples taken from the A Horizon, differentiating between the thin top layer surface samples and the deeper samples taken from a depth of 0–30 cm. The work was performed using a single collector ICP-MS apparatus.

2. Experimental

The contaminated industrial area studied was an experimental coking plant built in 1969. This was an experimental plant used for research over a period of 30 years and during this time bituminous coals from different countries were processed in it. The coking plant consisted of six ovens of different widths, and incorporating a coal blend station, a charging car, a pushing system, a coke quenching tower, and a tar distillation plant. Over the years, other sections were added, including a preheating station for the coal blends, gasworks, etc. A schematic map of the whole plant is shown in Fig. 1. On average, the quantity of coal carbonized was about 30 tons per day. The soil samples used in this study were taken just after the plant was closed down in 1999, at the sampling points indicated in Fig. 1. Seven distinct zones were differentiated: BLEND, next to the coal blending plant; PUSH, next to the coke pushing car; CBELT, under the coal conveyor belt; QUENCH, the coke quenching area; PHEAT, next to the coal preheating plant; TDIST, between the tar distillation plant and the gasometer; GAS, on the other side of the gasometer, and FAR, the area furthest from the coke oven battery. At every sampling point, two different types of sample were collected: the so called surface sample and the deep sample, both of them corresponding to the A Horizon. After the sampling points had been selected, vegetation from the area was removed by hand within a radius of 15 cm from the centre of the area sampled. The surface samples were taken with a spatula, at a maximum depth of approximately 4 mm. They were designated with the name of the sampling area, followed by the number of the sampling point (BLEND1, PUSH3, etc.). Deep undisturbed samples were taken with an Eikelkamp sampler, which meets the NED 5743 standard for sampling soils or sediments with volatile components. This instrument consists of a core sampler (for sampling cylinders of 5 cm diameter and 30 cm height) with liner tubes and soil sample containers. Every soil cylinder taken was cut into six slices, 5 cm in height, for analysis.

Before analysis, the samples were dried at 40 °C according to the standard ISO 11464. The >2 mm fraction was rejected from the surface samples and in the case of the deep samples, material >3 mm, stones, and other strange materials (plastics, roots, etc.) were also removed. The ash content was determined by combustion of the organic matter at 815 °C, and the coal, coke and other carbonaceous products derived from the carbonization of the coal from the soil samples were estimated by optical microscopy. The samples were prepared according to the standards for petrography analysis of carbonaceous materials, ISO 7404/2 (1985), and the identified components were determined by means of a point-count analysis following the ISO 7404/3 (1984) standard. Nine surface samples and two deep samples from the most representative points in each area were analyzed.

The total lead and isotope ratios were determined in the ashes of all the soil samples obtained at 500 °C. For the isotope ratio determinations, 0.05 g of ash mixed with 2 ml of HNO_3 (65% mass/volume) was extracted at 600 W for 6 min in a microwave oven. To determine the bulk lead content, an identical quantity of ash was totally dissolved in a two-step program. In the first step, 2 ml of $HNO_3 + 3$ ml of HF (48% mass/volume) were used to dissolve the sample over a period of 17 min at different intervals, employing a power of between 300 and 600 W. The second step consisted of adding 5 ml of HBO_3 to the solution and heating it in the microwave oven for 6 min at 600 W. The resulting solutions were filtered and diluted to 50 ml. The total lead and isotope ratio determinations

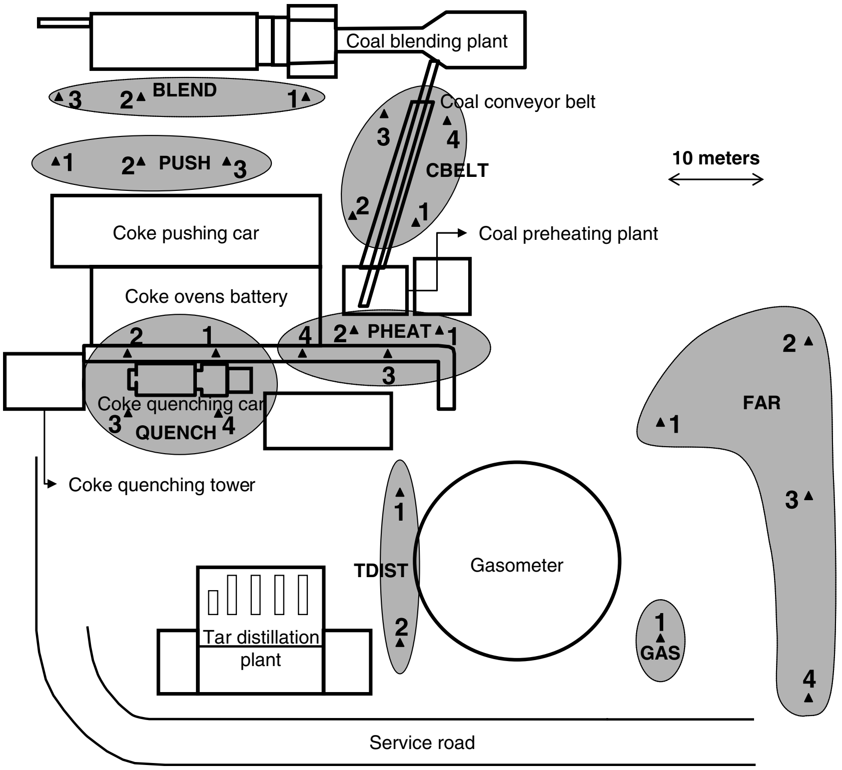

Fig. 1. Sampling points (▲) at the INCAR coking battery.

were carried out in an ICP-MS Hewlett–Packard model HP-4500. Thallium was used as internal standard. The isotopic ratios have been corrected for mass spectrometric fractionation effects on the basis of repeated measurements of the standard NIST SRM 981 (Natural Lead Isotope). In both the determination of total lead and the determination of isotope ratios two aliquots were analyzed and five replicate analyses were carried out for each aliquot. Different reference materials were used to validate the analytical method for lead determination: a contaminated soil from a carbonization plant (LGC6138) supplied by the Laboratory of the Government Chemist, United Kingdom and with a high certified lead content, 490 $\mu g\ g^{-1}$; a soil from a slightly contaminated site located in the Rocky Mountain Region of the USA (CRM026-050) with a certified value for lead concentration of 25.6 $\mu g\ g^{-1}$; a soil from an agricultural site located in California, San Joaquin Valley, USA (SRM2709) with a low lead content, 18.9 $\mu g\ g^{-1}$, and a coal standard sample (NIST SARM 20) supplied by the Bureau of Standards with a certified lead concentration of 26 $\mu g\ g^{-1}$.

The validity of the analytical method used in this study for total lead determination was assessed from the precision and accuracy of the results (Table 1). The precision of the analysis (SD_{Total}) depends on two independent sources of error, uncertainty in the sample preparation procedure (SD_{SP}) and instrumental precision (SD_{Instr}). These parameters are related in Eq. (1).

$$(SD_{Total})^2 = (SD_{SP})^2 + (SD_{Instr})^2 \quad (1)$$

SD_{Total} was evaluated by analysing eleven replicate samples of the reference material, SD_{Instr} was obtained by analysing one of the previously mentioned solutions eleven times in the equipment (ICP-MS) and SD_{SP} was calculated by means of Eq. (1). The accuracy of the proposed method was determined by comparing the results obtained with the certified value of the standard samples used.

3. Results

The soil samples taken from the A Horizon of the contaminated experimental coking battery area contained different proportions of carbonaceous material (Table 2) that are clearly related to the distance from the contamination source. High concentrations of coke, coal and tar were observed in samples taken from areas near the coking

Table 1
Accuracy and precision of the results obtained for total Pb determination by ICP-MS

Reference sample	SD_{Total}	SD_{Instr}	SD_{SP}	%RSD	X	X_{cert}	Dif. (%)
LGC6138	26.4	7.36	25.3	6.34	416	490	15

SD_{Total}: precision of the analysis; SD_{Instr}: instrumental precision; SD_{SP}: uncertainty in the sample preparation procedure; % RSD: relative standard deviation; X: obtained value; X_{cert}: certified value; Dif.: difference between the certified and the obtained values in percentage.

Table 2
Soil sample characterization

Sample	Distance from de coking ovens (m)	Depth (cm)	Petrographic analysis (% v)			Ash content (wt%)	Pb (μg g^{-1})
			Coal	Coke	Tar		
PUSH2	11.8	0	36.8	26.6	–	18.0	317 ± 8
		0–5	38.2	23.2	1.6		306 ± 8
		10–15	0.4	0.6	–		26 ± 1
		25–30	0.2	–	–		17 ± 1
BLEND2	17.6	0	11.0	6.6		43.9	103 ± 2
		0–5					54±
		10–15					11 ± 0
		25–30					5.7 ± 0.1
CBELT1	9.5	0	0.2	0.6		96.8	17 ± 0
		0–5					104 ± 2
		10–15					50±
		25–30					28 ± 1
CBELT4	20.5	0	5.4	6.0		64.3	181 ± 3
		0–5					103 ± 2
		10–15					9.5 ± 0.1
		25–30					11 ± 0
PHEAT1	13.0	0	29.0	15.8	7.6	25.3	349 ± 8
		0–5	10.6	17.0			233 ± 6
		10–15	5.8	5.6	1.2		238 ± 6
		25–30	30.2	15.8			136 ± 2
QUENCH3	7.0	0	20.8	46.2		14.5	230 ± 5
		0–5					101 ± 2
		10–15					64 ± 1
		25–30					46 ± 1
TDIST2	33.5	0	1.2	1.2		82.8	44 ± 1
		0–5					69 ± 1
		10–15					55 ± 1
		25–30					12 ± 1
FAR2	52.0	0	2.2	2.6		86.8	34 ± 1
		0–5					19 ± 0
		10–15					9.9 ± 0.1
		25–30					13 ± 0
Dutch Standard: Target-intervention							85–530

ovens (PUSH2, PHEAT1 and QUENCH3). In general, the soils with the lowest ash contents or the highest percentages of carbonaceous material were those from the PUSH and QUENCH areas (Table 2), where the presence of coal and coke was visible. Lead concentrations in the soil samples studied ranged from 17 μg g^{-1} to 349 μg g^{-1}. The sample considered as the background soil (FAR2) was found to have 34 μg g^{-1} of lead. The lowest value corresponds to a sample taken from a path covered with sand (CBELT1) and the highest to a sample corresponding to the preheating plant (PHEAT1), with a carbonaceous material content near to 50%. In general, a relationship can be observed upon comparing the total carbonaceous matter and the lead content in the soil samples (Fig. 2), indicating that the coal carbonization was responsible for an enhancement of the lead content in this soil.

The lead isotope ratios for the different samples and standards are given in Table 3. The results are denoted as the average value of five repetitions of the isotope analysis ± the standard deviation of these values. The RSD (relative standard deviation of the results) for the isotope ratio measurements are of the order of 0.4%; 0.2% and 0.2% for ^{204}Pb/^{208}Pb; ^{206}Pb/^{208}Pb and ^{207}Pb/^{208}Pb, respectively.

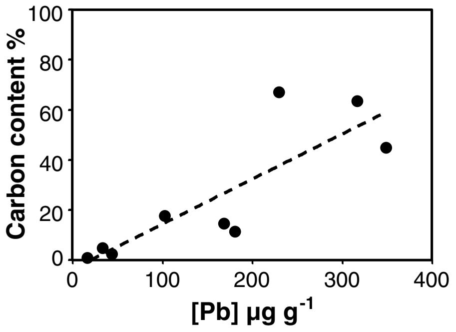

Fig. 2. Relationships between carbonaceous matter (coal + coke + solid tar) content and lead concentration.

Fig. 3 shows the ratio most commonly used in Pb pollution studies (^{206}Pb/^{207}Pb), for the samples taken at different points. The values of each sample are compared in Fig. 3

Table 3
Lead concentrations (μg g^{-1}) and lead isotope ratios for the different top-soil samples analyzed

Sample	[Pb]	204/208	206/208	207/208	206/207	208/206
PUSH2	317	0.0351 ± 0.0006	0.4737 ± 0.0002	0.4040 ± 0.0004	1.1725 ± 0.0003	2.1110 ± 0.0002
BLEND2	103	0.0353 ± 0.0002	0.4823 ± 0.0008	0.4031 ± 0.0006	1.1965 ± 0.0007	2.0734 ± 0.0008
CBELT1	17	0.0300 ± 0.0001	0.4839 ± 0.0009	0.4072 ± 0.0006	1.1884 ± 0.0008	2.0665 ± 0.0009
CBELT4	181	0.0313 ± 0.0003	0.4726 ± 0.0010	0.4055 ± 0.0006	1.1655 ± 0.0008	2.1160 ± 0.0010
PHEAT1	349	0.0290 ± 0.0001	0.4867 ± 0.0007	0.4066 ± 0.0008	1.1970 ± 0.0008	2.0547 ± 0.0007
QUENCH3	230	0.0356 ± 0.0006	0.4691 ± 0.0010	0.4055 ± 0.0009	1.1568 ± 0.0010	2.1317 ± 0.0010
TDIST2	44	0.0290 ± 0.0001	0.4794 ± 0.0008	0.4074 ± 0.0004	1.1767 ± 0.0006	2.0859 ± 0.0008
FAR2	34	0.0342 ± 0.0003	0.4709 ± 0.0005	0.4056 ± 0.0003	1.1610 ± 0.0004	2.1236 ± 0.0006
LGC6138	490	0.0298 ± 0.0001	0.4848 ± 0.0006	0.4078 ± 0.0008	1.1888 ± 0.0007	2.0627 ± 0.0006
CRM026-050	26	0.0336 ± 0.0001	0.5116 ± 0.0006	0.3966 ± 0.0004	1.2900 ± 0.0005	1.9547 ± 0.0006
SRM2709	19	0.0378 ± 0.0003	0.4916 ± 0.0010	0.4012 ± 0.0009	1.2253 ± 0.0010	2.0342 ± 0.0010

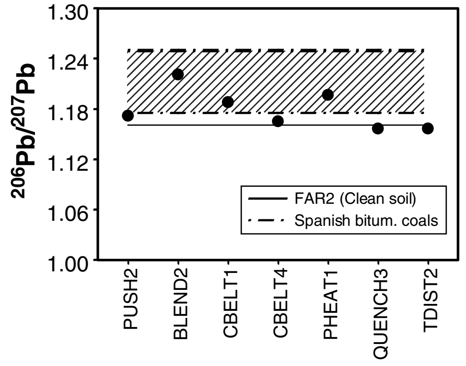

Fig. 3. Comparison of the ^{206}Pb/^{207}Pb ratios for the different sampling points with bituminous coals and the background soil. The numbers plotted indicate lead concentrations (μg g^{-1}) for the different samples.

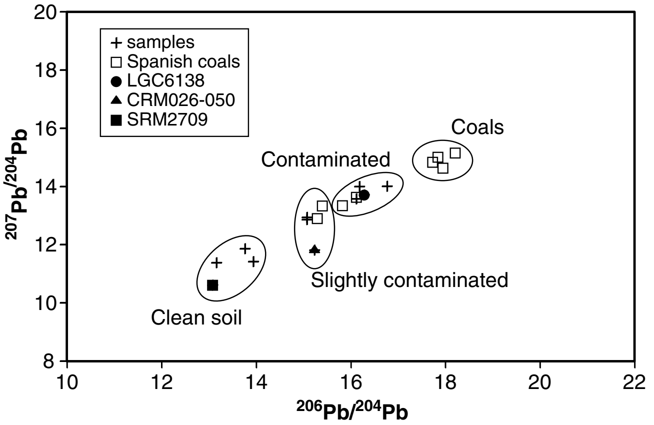

Fig. 4. ^{206}Pb/^{207}Pb/^{204}Pb plot for all the soil samples, reference soils and Spanish coals [15].

with the value of the background soil (FAR2), and with the range of bituminous coals from different areas in Spain [16]. The QUENCH3, PUSH2, CBELT4 and TDIST2 samples have isotope ratios that are similar to sample FAR2, which is used in this work as the background soil, whereas BLEND2, CBELT1 and PHEAT1 have ^{206}Pb/^{207}Pb ratios inside the bituminous coal range.

The use of a ^{206}Pb/^{207}Pb/^{204}Pb plot (Fig. 4) allows the U-derived ^{206}Pb and Th-derived ^{207}Pb isotopes to be normalised by the non-radiogenic isotope ^{204}Pb. In Fig. 4, the isotope ratios for the anthropogenic pollutants (coals), for the soils studied and for unpolluted soils, fall on a straight line, indicating the presence of only two lead sources, lead from coal and natural lead from the soil, whose isotope ratios fall at the ends of the line. The points plotted in Fig. 4 may be grouped into different sections, which, in turn, are associated with different types of samples or areas in the polluted soil. The first group which includes samples far from the coking furnaces, quenching and preheating zones, shows isotope ratio values similar to those of the standard agricultural soil used as reference (SRM2709) and the background soil FAR2. The second group is formed by samples from the furnace and conveyor belt areas. These samples have isotope values similar to the slightly contaminated standard (CRM026-050). The third group includes samples from the preheating and the gasometer areas. Isotope ratios for this group are close to those of a contaminated soil (LGC6138) and similar to the isotope ratios of Spanish coals [16]. These results corroborate the view that coal carbonization is the source of lead in the soil samples with the highest lead content.

After its deposition in the soil, lead may be mobilized to deeper layers and an evaluation of lead content variations and lead isotopic composition across the soil profile can be used to determine the extent of pollution [8,12]. Fig. 5 shows the variations in lead content and isotope ratios in representative samples from different areas of the soil. The concentration tendencies in the A Horizon with depth show that the lead content decreases with depth. The ^{206}Pb/^{207}Pb ratios were found to be generally lower in the samples from the thin surface layer soil and higher in the deepest soil layers. According to the data in Figs. 3 and 4, the highest ratios correspond to the coals and the lowest to the reference and background soils. Fig. 5 shows that lead from the coal has been transported to the bottom of the A Horizon layer. In the case of the PUSH2 sample, which was one of the samples with the highest lead content, a dramatic drop in lead concentration to less than 50 μg g^{-1} was accompanied by a rise in the ^{206}Pb/^{207}Pb ratio in the deeper samples. This suggests that the lead is contained in the topsoil and is not leached in significant

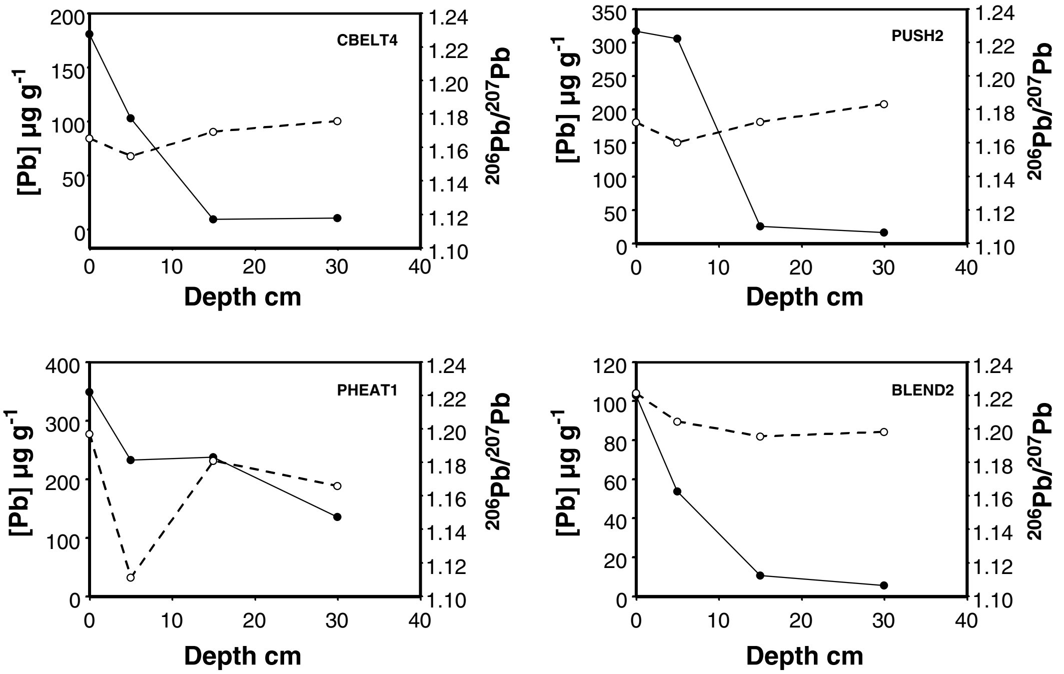

Fig. 5. Lead content (—) and ^{206}Pb/^{207}Pb ratio (- - -) for the profiles of different representative sampling points.

concentrations. It also indicates that the lead present in the lower level of the A Horizon mainly comes from the anthropogenic coal source. A similar trend was observed in CBELT4. However, in the PHEAT1 and BLEND2 samples the ^{206}Pb/^{207}Pb ratio at the deepest point of the profile is similar to, or even lower than, that of the surface sample. The low values found for the ^{206}Pb/^{207}Pb ratio were attributed to another source of lead. In the PHEAT1 area, wastes such as mineral/lubricating oils and diesel fuel from the maintenance and cleaning of the hydraulic systems were deposited.

4. Conclusions

An evaluation of the level of lead contamination and possible sources of pollution in the soil around the experimental coking plant used for research purposes over a period of 30 years has demonstrated that the lead concentration was higher in the area immediately around the coking plant than in the faraway soil. However, the lead concentrations in this soil were lower than the intervention limit values established for contaminated soils by Dutch Standards (530 $\mu g\ g^{-1}$). Lead isotope analysis reveals the existence of two main sources of lead, natural Pb and anthropogenic Pb, with some exceptions (e.g. PHEAT1) due to fugitive lead emissions from other activities related to plant maintenance operations and the use and handling of mineral/lubricant oils and diesel fuel. Most of the lead appears only in the thin top layer of the soil. Lead from carbonaceous materials deposited in the soil leaches down through the A Horizon in low proportions and in concentrations lower than those established as intervention values.

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