Impact of a semi-industrial coke processing plant in the surrounding surface soil. Part I: Trace element content

Mercedes Díaz-Somoano*, M. Antonia López-Antón, Isabel Suárez-Ruiz, Montserrat Calvo, Sonia Suárez, Roberto García, M. Rosa Martínez-Tarazona

Instituto Nacional del Carbón (CSIC)

Francisco Pintado Fe 26, 33011-Oviedo, Spain

*Corresponding author: mercedes@incar.csic.es. Phone: +34985119090, Fax: +34 985 297662

Abstract

Soil pollution by anthropogenic activities is an important environmental issue especially in industrialized countries. The objective of this study is to evaluate the environmental impact of a coal conversion plant on the surrounding soil by measuring the spatial distribution of particulate organic carbon and determining the concentration of trace elements (part I) and PAHs (part II). The results indicate that the surface soil present an increase in the content of organic particulates with values exceeding 80% vol. at the centre of the coking plant facilities. The concentrations rapidly decrease as the distance from the plant increases. Although concentrations of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn in most cases did not exceed the environmental limits, a clear relationship was established between the presence of some of these elements and the high values of particulate organic carbon content found in the proximity of the plant.

Keywords: Organic Particulates; Trace elements; Soil contamination; Coking plant.

1. Introduction

Industrial activities releasing metals or organic particulates impact surrounding soils [1-5]. These pollutants pose a significant risk for health and the natural environment. Coals contain most of the elements of the periodic table in different forms and concentrations [6]. During the coal conversion processes these elements can be emitted to the atmosphere in gas phase or associated with fine particles and they are then deposited in surrounding waters and soils. The anthropogenic activities related to coal and their impact on soils began to cause concern from so long ago as the middle of the 19th century (e.g., [7.-11]). Coking activities are among the most polluting processes related to coal utilization. Coking processes involve coal and coke handling (e.g., transport and blending), charging, carbonisation, coke pushing and quenching, battery underfiring, gas cleaning, and the processing of by-products. The source of pollution can be broadly classified as either continuous or fugitive [12-13]. Continuous emissions are those that occur throughout the entire carbonisation cycle, whereas the more complex fugitive emissions are related to specific operations such as charging, pushing, leakages, etc. In the case of continuous emissions, the main pollutants consist predominantly of particulates, sulphur, nitrogen oxides and gaseous toxic metals, such as mercury. Fugitive emissions may also involve heavy metals, polycyclic aromatic hydrocarbons (PAHs) and other volatile organic compounds (VOCs), particulates and hydrogen sulphide. All of these contaminants are dispersed in the surface soil of the surrounding areas through dry and wet deposition [14].

About 300,000 sites across the EU have been identified as definitely or potentially contaminated, but, according to the best estimation, there are about 1.5 million contaminated areas [15] due to different industrial activities. In recent years a number of studies have been carried out in order to establish baseline values, e.g., for PAHs and trace elements in soils, some of which have been

addressed towards an evaluation of the possible contamination of soil by human activities [11, 16-20].

The present study evaluates the impact of a semi-industrial coking plant, located near Oviedo (North of Spain), on the surrounding soil. This experimental installation allows the possibility of studying a well-known source of pollution in many industrial processes, as all the different kinds of work carried out over the years are well documented. In addition, the location is in a rural area without other significant sources of pollution. The impact of the coking plant on the surrounding soil is evaluated taking into consideration: i) the volume of organic particulates (particulate organic carbon, POC) present in the soil, ii) the amount of continuous emissions, mainly related to coal handling, coke and sub-products, and iii) fugitive emissions related to the heavy metals present as trace elements of environmental and health concern (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, V, and Zn).

2. Materials and Methods

2.1. Studied Area and the coking plant

The studied area cover the soil surrounding the location of the coking plant (Fig. 1). This plant was in operation for 30 years. Before the construction of the plant the area chosen for its location was a rural area totally free from other sources of industrial pollution. The coking plant was equipped with six ovens of different widths, which carbonised around 30 tonnes of blended coals per day. The installation also incorporated a coal blending station, coal hoppers, a charging car, a pushing system, a coke quenching tower, a coke classification plant, a coke fines pond, a tar distillation plant for the separation of various tar fractions, a gasometer and a gas chimney. The total area covered by the coking plant activities amounted to around 9,000 m².

2.2. Soil sampling and sample preparation

Soil samples were taken just after the closure of the coking plant and the location of the sampled points is shown on the schematic map in Fig. 1. Based on the different activities carried out in the coking plant, nine zones were selected as being of special interest. These zones include: BLEND, next to the coal blending plant; CBELT, the area under the coal conveyor belt, between the coal blending and the coal preheating plants; PHEAT, next to and around the coal preheating plant; PUSH, next to the coke pushing car; INTER5, located between the BLEND and PUSH areas; QUENCH, the coke quenching area close to the coke oven battery; TDIST, the area between the tar distillation plant and the gasometer; GAS, on the opposite side of the gasometer, EXTERNAL and FAR, the areas farthest away from the coke oven battery which are used as reference samples after checking the similar results obtained for these samples to faraway others.

In each area, several points were sampled (Fig. 1), and, in each sampled point, two different sets of samples from the soil were collected: one taken from the top (0-4 mm), called O horizon sample, and a second one called A horizon sample (taken from a depth of up to 30 cm depth). Before sampling, the vegetation in the area was removed by hand. The O horizon samples were taken with a spatula. The A horizon undisturbed samples were taken using an Eikelkamp sampler, to meet the NEN 5743 (1995) standard for sampling soils and sediments containing volatile components. This device consists of a core sampler with sampling cylinders 5 cm in diameter and 30 cm in height, and is fitted with liner tubes and soil sample containers. Every full cylinder was cut into 6 slices, 5 cm in height, for analysis. After collection, the soil samples were refrigerated (4 °C) under argon in glass bottles and covered with plastic caps (O horizon samples) or in sealed PVC containers (A horizon samples). Before being subjected to physico-chemical analysis, the O horizon samples were dried at 40 °C. In order to obtain samples of a suitable size for analysis, the classical method of coning-and-quartering was used. For the determination of

trace elements, any fraction over 2 mm was rejected and any fraction less than 2 mm was divided again using a 50 μm sieve. The rejected material was ground to < 50 μm . Both fractions, > 50 and < 50 μm , were analysed in this study.

2.3. Petrographic characterization

Petrographic analyses were carried out on representative portions of all the O horizon samples (0-4 mm) and for selected A horizon samples (i.e. representative portions of the slices obtained at three different depths: 0-5 cm, 10-15 cm, and 25-30 cm). The A horizon samples chosen for petrographic analysis were taken in general, from the visually most polluted areas such as QUENCH, PHEAT, PUSH and BLEND (Fig. 1). In all cases, the preparation of the samples for petrographic analysis was conducted following a modified procedure of the ISO 7404/2 (1985) standard. The petrographic composition was determined in terms of volume percentages of coal, coke and solid tar particles present in the O horizon samples and in the selected A horizon samples by means of a point counter coupled to an optical microscope (Zeiss Axioplan microscope) (ISO 7404/3, 1994). A 50x oil immersion objective, with polarized light and a retarder plate incorporated into the microscope system were used during the analysis to enhance the contrast between the components.

2.4. Chemical and Ash Analysis.

The total ash content (HTA) of the soil samples was obtained by combustion of the organic matter at 815 °C until constant mass, following the ISO 1171 (1997)/UNE 32004 (1984) norms. The concentrations of minor and major oxides (Al, Ce, Fe, K, Mg, Na, Si, and Ti) were determined using X-ray fluorescence spectroscopy (XRF). The XRF apparatus was a sequential

wavelength-dispersive Siemens SRS 3000 X-ray spectrometer equipped with a Rh X-ray tube, a 58 position sample turntable, and a flow counter detector. Prior to the XRF analysis the ashes obtained from the soil samples were subjected to a fusion step using lithium tetraborate in order to obtain sample beads for analysis. The device used to prepare the sample was a Philips Perl' X3 automatic fused bead machine.

The mineral compositions were identified using X-ray diffraction (XRD) after the elimination of organic matter by means of low temperature oxygen plasma (LTA). The equipment used was a Siemens D5000 diffractometer equipped with a graphite diffracted-beam monochromator. The samples were scanned between 5 and 60° using Cu K α radiation.

2.5. Trace Element Analysis

Eleven trace elements (Be, Cr, Mn, Co, Ni, As, Se, Cd, Sb, Pb, and Hg) were analyzed for their potential harmful effects on the ecosystem. Other elements of interest for human health, such as V, Cu, and Zn, were also evaluated.

The trace elements were extracted from the soil samples by acid digestion in a microwave oven, using 2 ml of nitric acid and heating for 10 minutes at a maximum power of 600 W. In the case of Sb, total dissolution of the sample was necessary in order to extract the element from the sample. A two-step microwave program using 4 ml of HF plus 2 ml of HNO₃ and heating for 17 minutes in a power range of between 300-600 W was employed. Teflon high pressure digestion vessels (HPV80) were used in the process. As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, V, and Zn were determined by ICP-MS (HP 4500). Se was determined by ICP-MS, preceded by hydride generation (HG-ICP-MS), following the procedure developed by [21], while Hg was analyzed using an automatic mercury analyser (LECO AMA 254). Samples with high concentrations of Mn were analyzed by atomic absorption spectrometry (AAS), using an IL Video 12 atomic

absorption spectrometer. Analysis control quality was assured by using certified reference soil samples.

3. Results and discussion

3.1. Concentration of particulate organic carbon in the soil

Particulate organic carbon found in the O horizon soil surrounding the coking plant (Fig. 1) was mainly derived from the carbonization process. Microscopic analysis show that the bulk of the particulate organic carbon is made up of coal (bituminous rank or medium coal rank), coke displaying all types of optical textures and structures (from fine to coarse mosaic, ribbons, domains, pyrolytic carbon), and solid tars (isotropic and anisotropic). These organic particulates were found in almost all of the analysed samples in variable amounts ranging from 0.9 to 92.3% vol. in the O horizon samples (Table 1) and up to 93.6% in the A horizon samples (Table 2), the remaining fraction being inorganic material. Occasionally, traces of chars (small cenosphere-type), from coal combustion in the heating boilers of the buildings closest to the coking plant, were also found.

3.1.1. O horizon samples (0-4 mm depth)

The organic particulate contents of the O horizon samples are included in Table 1. The distribution and types of organic carbon particulates vary across the studied surface depending on the type of material handled in the sampled area, the process being undertaken when the coking battery was active, and the proximity of the investigated area to the point at which a particular activity was being carried out. Four main levels of concentration of particulate organic carbon (POC) can be described:

i) Level of POC concentration $\geq 80\%$ vol. It contains the most highly contaminated samples and includes all the O horizon samples from the QUENCH area. The concentration of organic particulates ranges between 79.6 and 92.0%, with a clear predominance of coke over coal particles (coke/coal ratio between 1.0 and 2.4, Table 1). Solid tar particles were also found in lower concentrations (0.2-3.2%). Samples from PHEAT4 and PHEAT3 (coal preheating area) are included in this group also, with a predominance of coke particulates (Table 1). The surface located behind the coke ovens close to the coal hoppers (PUSH1) displays a high content of coal particulates (coke/coal ratio: 0.2, Table 1).

ii) Level of POC concentration in the 50-80% vol. range. Most of sampled point from PUSH, BLEND and INTER areas are located in this group (Table 1). Coal particulates are then the predominant type (coke/coal ratio is from 0.6 to 0.8) because of the intense activity related to coal handling in those areas (mainly near to coal hoppers and the coal blending plant).

iii) Level of POC concentration in the 20-50% vol. range. The content of coal and coke particulates was found to be variable (see coke/coal ratio in Table 1) and mainly related to proximity to the focus of coal handling. The areas of coal handling (BLEND, CBELT) and coal preheating (PHEAT) are included in this category. Solid tar particles were found in amounts lower than 1.0% vol. although the PHEAT2 and, by extension, PHEAT3 and PHEAT4 sites showed significant solid tar particulate contents. This is because the PHEAT area is located inside the perimeter of the preheating plant activities and the sampled points are very close to the zones in which the preheated coal was loaded into the coke ovens. The temperature of the preheated coal was $\sim 200^\circ\text{C}$ and, therefore, the generation of tars contributing to soil pollution in the area of the coal preheating plant with a concomitant increase in the total content of organic particulates was to be expected. In addition the maintenance and cleaning operations carried out in those systems over the years, led to systematic leakages of liquid tars onto the ground

impregnating the soil surrounding the preheating plant. This explains the percentages of solid tar particulates found in these samples, and by extension in PUSH4 site (Table 1).

iv) Level of POC concentration $\leq 20\%$ vol. Areas such as EXTERNAL, FAR, TDIST, and GAS, together with CBELT1 and CBELT4, all located at the most external points of the coking plant site (Table 1) are included in this range of contamination by organic particulates. In these areas the coke/coal ratio is always higher than 1 (Table 1), showing a pollution mainly due to coke particulates. Here, the content in solid tar particulates is the lowest or even zero. TDIST1 site was an exception (soil tar content is 1.4 % vol., Table 1) due to its proximity to the tar distillation plant, the areas where the tar was transported, and the gas pipes regularly cleaned.

The integration of these results is included in Fig. 1 that shows the distribution of the total POC according to these 4 levels of organic particulates concentration. The lines that demarcate the different levels of concentration of POC have been estimated up to the area in which the tar distillation plant was located and beyond the location of the coke fines pond, in accordance with the trends of POC concentration. The high concentration in POC found in the tar distillation plant and coke fines pond is probably due to the coke particulates derived from coke handling. Moreover, taking into account that currently there is an open coal storage area next to the old coal blending plant, the concentration of coal particulates in that area may even exceed 20% vol.

3.1.2. A horizon profile (0-30 cm depth)

The distribution of organic particulates with increasing depth in the A Horizon is shown in Table 2. For comparison purposes, data for the corresponding O horizon samples are also included. In the A horizon samples analysed, particulate organic carbon was found, although, in some cases, only at the level of traces which is not reflected in the quantitative analysis. The POC contents

tend to decrease with depth in BLEND1, BLEND4, EXTERNAL1 and FAR2 sites (Table 2), but there are some exceptions linked to the different activities carried out in the studied area.

Down to a depth of 5 cm, the organic particulate content is significant to different degrees at all sampled points. At this depth, all the soil samples still display a high content of POC (QUENCH3, PUSH4, PUSH2, PHEAT1, CBELT4 and INTER5), with values of coke and coal particulates varying between ~20 and ~94% vol. (Table 2). Noticeable is also the high concentration of coal particulates (~20% vol.) in TDIST2 sample (Table 2), even higher at 10-15 cm depth than in its O horizon sample (< 2% vol.) (Table 2). This is due to the coal-fuelled forge installed in this site, next to which coal was piled up ready for use.

Solid tar particulate contents were found to be relatively high in some areas (e.g., QUENCH3, PUSH4, BLEND2, and PHEAT1, Table 2) at this depth, although their global concentration decreases with depth. The high tar content found in QUENCH and PHEAT sites at this depth and at 10-15 cm (Table 2) is due to its location close to the sources where the coals were carbonized and heated respectively, with the subsequent generation of tars over the years. Values of solid tar concentration in the PUSH4 site at this depth and at deeper levels of A horizon (Table 2) were produced by leaks during the maintenance and cleaning operations of the coke ovens and the pre-heating plant. The solid tar concentrations of 2.6 % vol. (Table 2) in the BLEND2 site (0-5 cm. depth) has been attributed to the presence in this area of a buried box culvert used to recover liquid tars resulting from the cleaning operations in the pipes and tubes.

Samples from the cores, at depths of 10-15 cm, show a great variability in POC content. Most of the sampled areas show a significant decrease in organic particulate content (Table 2), with a maximum of 4.3% vol. for CBELT1. The solid tar contents at these depths are almost zero, with the exception of sample BLEND2. Although most of the areas are located inside the field of the coking carbonization activities, they are far away from the focus of coke making and handling.

3.2. Inorganic fraction of O horizon, (0-4 mm depth): Ash content and ash composition.

The ash content (high temperature ashes, HTA) of the soil samples (O horizon samples, 0-4 mm depth), and their composition is shown in Table 3. The base/acid and silica/alumina ratios for the whole O horizon samples, and the ash content for the two granulometric fractions (<50 μm and >50 μm) of the surface samples are also included in this table. As expected, the ash content obtained for the whole samples confirms the amount of inorganic material determined by petrographic analysis with a good linear correlation ($r = 0.95$). Thus, samples with the lowest ash contents (10-25%) are those from the PUSH and QUENCH sites, which contained the highest percentages of total organic particulates (Table 1). Higher ash contents were found in the BLEND and PHEAT sampledg areas (14-64 %). The soil samples with the highest ash contents are TDIST, GAS and FAR (82-88%, Table 3). These sites are the furthest away from the coking ovens.

SiO_2 , Al_2O_3 and Fe_2O_3 are the predominant oxides (Table 3) present in the whole samples. In general, the highest Al_2O_3 and Fe_2O_3 and the lowest SiO_2 contents are found in the areas with the highest POC contents (QUENCH, PUSH and PHEAT). Clays, feldspars and aluminium silicates are also commonly found in coals. The highest SiO_2 and the lowest Al_2O_3 contents and, therefore, the highest silica/alumina ratios (Table 3) were found in the areas with relatively low concentrations of POC such as FAR, GAS, TDIST, and CBELT. The corresponding base/acid ratio results are shown in Table 3. In the areas with a high concentration of organic particulates (QUENCH, PHEAT, PUSH and BLEND) this ratio tends to increase mainly because of the significant increase in CaO , K_2O , Na_2O and especially Fe_2O_3 contents (Table 3).

X-ray Diffraction analysis was performed on the low temperature ashes of the <50 µm fraction in the search for primary minerals. Quartz (SiO₂) was identified in all of the samples and is the main component of the inorganic fraction. Although the minerals identified varied from one sample to another, the most abundant mineral in the samples, with low amounts of organic particulates, was quartz (CBELT1, TDIST2 and FAR2), with lower proportions of kaolinite and aluminosilicates (i.e. CBELT4), and, in some cases, with high concentrations of carbonates. In the samples from the areas highly contaminated by organic particulates other clay minerals such as illite, and calcium, magnesium and iron minerals, were also identified (BLEND2).

3.3. Trace element concentration in the soil.

3.3.1. Accuracy and precision of the analytical method

The accuracy of the analytical method was tested by determining the trace metal content in three standard reference samples: i) LGC6138, a soil sample from a contaminated carbonisation site; ii) RTC-CRM026-050, a soil sample from a slightly contaminated site, and iii) SRM 2709, an agricultural soil sample. Table 4 shows the average value of 11 replicate determinations of the metals in the standard samples, the differences between the certificate value and the results obtained being lower than 10% for the measured elements except in the case of Co, Cd and Sb. This confirms the good accuracy of the results.

The precision of the analysis can be evaluated from the results of standard deviation (SD) and relative standard deviations (%RSD) (Table 4). SD was evaluated by analysing 11 replicate samples of the above-mentioned reference materials. To express the RSD as a percentage it was calculated by dividing the standard deviation by the average measurement and then multiplying by 100. RSD values lower than 10% were found for most of the elements. The only exceptions were Cu and As with RSD values close to 12 %.

3.3.2. Trace element analysis in the O horizon samples (0-4mm depth)

Table 5 shows the results obtained from the analysis of trace metals present in the O horizon samples (0-4 mm depth). At the level of trace elements, one of the most difficult problems involved in assessing the contamination of a soil is to establish what level can be considered as a clean soil. Taking into account factors such as distance from the coking ovens and the organic particulate contents, the sample selected in this study as a reference sample to establish the background level was FAR2. The average concentrations of trace elements in the different sampled sites compared to the background level for all the elements studied and compared to the action values of the Dutch Standard for elements included in Table 5 are shown in Figs.2 and 3. According to the results found for the O horizon samples, the elements can be divided into two different categories. The first group includes elements with concentrations that exceed the action value established by the Dutch standard in only a few samples (Table 5). This is the case of Cu, Hg, Pb and Zn, whereas As, Cd, Cr, Co and Ni are elements whose concentrations in all cases are below the action values. When compared to the background concentrations, most of the elements (Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se and Zn) exceed the concentrations of the sample considered as a “clean soil”, although elements such as As, Be, Co, Mn and V are present, in several cases, in lower concentrations in the contaminated soil samples than in the sample referred to as background. Among these elements, only As and Co are included in the Dutch standard and, for them the concentrations in the background sample are lower than / or very similar to the optimum value (Table 5). It should be pointed out that concentrations above the background level were more frequently found in the areas with the highest organic particulate contents (>50 % vol.), such as PUSH, PHEAT and QUENCH.

The concentrations of Hg, in most of the samples, range from 0.04 to 1.30 $\mu\text{g g}^{-1}$, whereas the optimum and action values of the Dutch standard limits are set at 0.3 and 10 $\mu\text{g g}^{-1}$. There was only one exception: a sample located between the tar distillation plant and the gas container, TDIST1, which showed a significantly high mercury concentration of 19.9 $\mu\text{g g}^{-1}$. However, the samples taken from the proximity of this sampled site had much lower concentrations of Hg. The high value of Hg found in the O horizon sample of TDIST1 was probably due to the leaks occurred during the cleaning of the pipes conducting gases from the coke ovens to the gasometer. These gases contained products such as naphtha, among other hydrocarbons, that with the passing of time and in cold periods (winter) tended to condense on the inner walls of the pipes. It is known that mercury volatilizes with temperature and tends to concentrate in the gases generated during the coal carbonization process. Richaud et al. [22] observed the presence of 0.15 ppm of mercury in a coal tar pitch, which pointed to the organometallic retention of mercury in this fraction. In the present case, the systematic (every ten days) cleaning of the pipes and the corresponding leakages of the products into the ground led to the high Hg concentration in the soil of this area.

Most of the samples show a Cu concentration between the optimum and action values (Fig. 2). The exceptions are samples PUSH3 and PHEAT3, whose Cu concentrations exceeded the action value. The fact that higher concentrations of this element were found in sampling points located near the coking ovens is in accordance with previously reported [23] high emissions of Pb and Cu in the ascension pipe. The Zn concentrations (Fig. 3) indicate pollution in three areas: PUSH, CBELT and PHEAT. The presence of working benches during the installation of the pipes and other parts of the coal preheating plant and the scratching operation involved in making galvanized tubes could have given rise to enhanced Zn depositions at these sampled points. The highest concentrations of Pb are found in the PUSH, BLEND, PHEAT and QUENCH areas, but

always within the optimum-action range, with the exception of sample PHEAT3, whose Pb concentration exceeded the action value (Fig. 3). The origin of this relatively high Pb content is uncertain and may have been due to the combined effect of various sources: emissions during pushing and quenching [17, 25], pollution from the road traffic around the area or facility maintenance (e.g., painting), and almost certainly to the high contents of coal and coke in the sample (Table 1).

Table 6 shows the distribution trend of the heavy metals in relation to the described levels of POC concentration. Thus, the areas with a POC concentration $> 80\%$ vol. show the highest values for Co, Cr, Cu, Mn, Ni, Pb and V followed by Cd, Hg, Sb and Se. However, these last four trace elements have their highest concentrations at the sampling points with POC concentrations between 80 and 50% vol. As shows the highest value in the area whose organic particulate content is between 50 and 20%, whereas the areas less contaminated with organic particulates showed the highest Be and Zn values. In comparison with data reported by Swaine [6] for some trace element concentrations in world coals (Table 6), some of the sampled sites were highly enriched in trace elements, such as Cu and Pb (QUENCH, PHEAT, PUSH, BLEND and CBELT areas) and so contamination by these heavy metals can be considered high. Other sites were locally enriched in Mn and Sb (PHEAT areas) and in Se (PUSH).

3.3.3. Trace elements along the A Horizon profile

The results from the analysis of samples taken from along the A Horizon were also evaluated in order to: i) investigate the evolutionary trend of trace element concentration with depth, ii) determine the contribution of organic particulates to trace element content, and iii) ascertain whether trace elements leach. The variation in trace element concentrations along the profile of the A Horizon in representative samples taken from the contaminated site is shown in Fig. 4.

Different trends can be observed for each element studied and at each sampled point. In some samples the concentrations of the trace elements decrease with the depth of the profile. This is generally associated with a decrease in the concentration of organic particulates (Table 2). An element that is representative of this behaviour is Pb, but Cd, Cu, Hg, Se, and Zn also follow the same tendency at most of the sampling points. In other cases, the trace element concentrations increase with the depth of the profile and/or as the organic particulate concentration decreases. This is the case of V at some of the sampled points. For the other elements, the concentrations are similar along the whole profile and do not follow a clear trend or differ noticeably from sample to sample.

Determination of the trace element concentrations in the representative samples taken from the A Horizon profile indicates that, as in the case of the O horizon samples, if the average value of the whole profile is taken into account, the concentrations of Co, Cr, and Ni, are below the optimum value of the Dutch Standard; As, Cd, Cu, Hg and Pb are below the action value and only in the case of Zn do some deep samples reach the level of the action values (Table 5). The variation in concentration depends not only on the element under consideration but also on the location of the sampling points, as these are situated at different distances from the main contamination focus (Fig. 1) and they differ in terms of soil, carbonaceous matter and mineral matter composition. If the presence of coal in the sample is taken into account, it can be observed that Cd, Cu, Hg, Pb, Se, and Zn are concentrated in the samples enriched in coal particulates. In general, the deepest sample taken from the A Horizon consists mainly of clay minerals, and so the presence of these elements must be due to one of two reasons: either they were originally present in the inorganic fraction, or they were captured after the elements had leached through the soil. Only at some points is the V element clearly concentrated at the deepest point.

Conclusions

The environmental impact of a coking plant in operation for more than 30 years upon the surrounding surface soil has been evaluated in terms of organic particulates and heavy metal concentration.

The entire area shows the presence of POC in varying amounts depending on the proximity of each sampled area to the centre of the coke oven activities, coal and coke handling, and on the depth of the A Horizon. The continuous work carried out in this coking plant caused the surrounding soil to be enriched with the coal, coke and solid tar particulate concentrations with values of up to 92% vol. in the O horizon samples. According to the organic particle content four levels have been identified: >80, 80-50, 50-20, and <20% vol. of POC. Fugitive contamination was also frequent and it was due to leakages in the systems and to cleaning and maintenance work. This type of contamination is reflected in the higher solid tar particulate contents. Along the soil profile (A horizon) most of the sites around the coking plant clearly show a reduction in POC content.

The concentration of trace elements (As, Cd, Co, Cr, Cu Hg, Ni, Pb and Zn) in the soil was found to be mostly below the action values of the Dutch Standards. The areas with a high POC content (coke ovens, preheating plant, coke and coal handling) show a clear enrichment in concentrations of heavy metals such as Cu, Mn, Pb and Sb. In general the presence of Cd, Cu, Hg, Pb, Se, and Zn is related to higher values of particulate organic carbon content. A clear relationship can be established between high POC and high metal content with the areas implicated in coal or coke handling.

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Figure captions

Figure 1. Schematic map of the surface ($\sim 8000\text{-}10000\text{ m}^2$) covered by the activities of the coking plant and location of the sampling points (▲) and areas. Spatial distribution of the organic particulate content (coal, coke and solid tars) as identified by optical microscopy and according to the levels of concentration established for the O horizon samples (0-4 mm depth).

Figure 2. Spatial distribution of As, Be, Cd, Co, Cr, Cu and Hg concentrations in the O horizon samples of the soil (0-4 mm depth).

Figure 3. Spatial distribution of Mn, Ni, Pb, Se, Sb, V and Zn concentrations in the O horizon samples of the soil (0-4 mm depth).

Figure 4. Vertical profile of trace elements along the A horizon.

Table 1. Petrographic composition of the O horizon (0 cm depth) and coke/coal ratio for the sampled sites. The measured distance of each sampled point to the Coke Ovens Battery (see Figure 2 for reference) is also included.

Zone	Sample Reference	Distance from the Coke Ovens Battery (m)	Coal (vol. %)	Coke (vol. %)	Solid Tar (vol. %)	Inorganics (vol. %)	Coke / Coal Ratio
1	QUENCH 1	5	27.4	60.7	0.4	11.5	2.2
1	QUENCH 2	9	37.3	49.3	0.2	13.2	1.3
1	QUENCH 3	12	22.4	54.0	3.2	20.4	2.4
1	QUENCH 4	14	36.7	52.5	0.3	10.5	1.4
2	PUSH 1	22	77.1	12.0	0.4	10.5	0.2
2	PUSH 2	16	36.8	26.6	0.0	36.6	0.7
2	PUSH 3	15	37.5	30.3	0.2	32.0	0.8
2	PUSH 4	18	33.0	28.8	6.2	32.0	0.9
3	PHEAT 1	25	29.0	15.8	0.0	55.2	0.5
3	PHEAT 2	16	9.4	11.8	1.2	77.6	1.3
3	PHEAT 3	20	32.6	46.1	1.3	20.0	1.4
3	PHEAT 4	13	45.8	43.8	2.7	7.6	1.0
4	BLEND 1	25	19.0	19.7	0.1	61.1	1.0
4	BLEND 2	23	15.3	7.5	0.3	77.0	0.5
4	BLEND 3	26	40.0	23.9	0.5	35.6	0.6
4	BLEND 4	23	14.4	16.0	0.7	68.9	1.1
4-5	INTER 5	19	23.6	28.6	0.6	47.2	1.2
5	CBELT 1	24	0.3	0.6	0.0	99.1	1.7
5	CBELT 2	19	16.4	12.3	0.4	70.9	0.7
5	CBELT 3	27	22.3	24.1	0.1	53.5	1.1
5	CBELT 4	32	5.4	6.0	0.0	88.6	1.1
6	TDIST 1	28	1.6	6.9	1.4	90.1	4.4
6	TDIST 2	41	1.4	2.5	0.5	95.6	1.8
7	GAS 1	59	0.7	2.2	0.2	96.9	3.1
8	FAR 1	49	2.0	4.1	0.0	93.9	2.1
8	FAR 2	63	2.2	2.6	0.0	95.2	1.2
8	FAR 3	66	0.7	2.0	0.0	97.2	2.8
8	FAR 4	75	1.9	2.3	0.0	95.8	1.2
9	EXTERNAL 1	86	1.3	4.4	0.0	94.3	3.4

Table 2. Petrographic composition of the soil profile along A Horizon (0-30 cm depth) and coke/coal ratio for the sampled sites.

Sample Reference	Depth (cm)	Coal (vol. %)	Coke (vol. %)	Solid Tar (vol. %)	Inorganics (vol. %)	Coke / Coal Ratio
BLEND 1	Surface	19.0	19.7	0.1	61.2	1.0
	0-5	8.9	10.6	0.0	80.6	1.2
	10-15	0.0	2.0	0.0	98.0	
	25-30	0.5	0.0	0.0	99.5	0.0
BLEND 2	Surface	15.3	7.5	0.3	77.0	0.5
	0-5	13.7	12.9	2.6	70.9	0.9
	10-15	0.9	0.3	0.4	98.4	0.3
	25-30	0.2	0.0	0.0	99.8	0.0
BLEND 4	Surface	14.4	16.0	0.7	68.9	1.1
	0-5	4.4	2.7	0.0	92.9	0.6
	10-15	0.6	0.0	0.0	99.4	0.0
	25-30	0.2	0.1	0.0	99.7	0.5
INTER 5	Surface	23.6	28.6	0.6	47.2	1.2
	0-5	15.8	18.2	0.5	65.5	1.2
	10-15	0.0	0.4	0.0	99.6	
	25-30	0.0	0.0	0.0	100.0	
PUSH 2	Surface	36.8	26.6	0.0	36.6	0.7
	0-5	34.2	26.6	0.4	38.8	0.8
	10-15	1.3	0.4	0.0	98.3	0.3
	25-30	0.1	0.0	0.0	99.9	0.0
PUSH 4	Surface	33.0	28.8	6.2	32.0	0.9
	0-5	24.2	25.6	3.2	47.0	1.1
	10-15	22.4	21.4	2.4	53.8	1.0
	25-30	4.4	6.7	0.7	88.2	1.5
QUENCH 3	Surface	22.4	54.0	3.2	20.4	2.4
	0-5	36.2	54.4	3.0	6.4	1.5
	10-15	37.0	49.5	1.5	12.0	1.3
	25-30	0.9	1.4	0.9	96.7	1.5
CBELT 1	Surface	0.3	0.6	0.0	99.1	1.7
	0-5	7.0	9.4	0.0	83.6	1.3
	10-15	2.3	2.0	0.0	95.7	0.9
	25-30	0.3	0.3	0.0	99.4	1.0
CBELT 4	Surface	5.4	6.0	0.0	88.6	1.1
	0-5	18.4	27.4	0.4	53.8	1.5
	10-15	0.0	0.0	0.0	100.0	
PHEAT 1	Surface	29.0	15.8	0.0	55.2	0.5
	0-5	12.2	16.2	0.4	71.2	1.3
	10-15	5.3	3.9	0.6	90.3	0.7
	25-30	31.0	17.5	0.2	51.3	0.6
TDIST 2	Surface	1.4	2.5	0.5	95.6	1.8
	0-5	20.4	0.4	0.0	79.2	0.0
	10-15	20.7	1.6	0.0	77.7	0.1
	25-30	0.0	0.0	0.0	100.0	
FAR 2	Surface	2.2	2.6	0.0	95.2	1.2
	0-5	0.5	0.4	0.0	99.1	0.7
	10-15	0.0	0.3	0.0	99.7	
EXTERNAL 1	Surface	1.3	4.3	0.0	94.4	3.3
	0-5	2.8	1.0	0.0	96.2	0.4
	10-15	0.5	0.1	0.1	99.3	0.2
	25-30	0.4	0.2	0.0	99.4	0.5

Table 3. Ash content, ash composition, base/acid and silica/ alumina ratios for the O horizon samples. The ash contents for the granulometric fractions (< 50 μm and > 50 μm fractions) of the soil samples are also included.

Sample Reference	Ash (wt.%, db)	Al ₂ O ₃ (wt.%)	SiO ₂ (wt.%)	CaO (wt.%)	Fe ₂ O ₃ (wt.%)	MgO (wt.%)	K ₂ O (wt.%)	Na ₂ O (wt.%)	TiO ₂ (wt.%)	Base/ Acid ratio	Silica/ Alumina ratio	<50 μm Ash (wt.%, db)	>50 μm Ash (wt.%, db)
QUENCH 1	15.3	20.50	40.00	1.32	33.10	1.53	1.20	0.75	1.12	0.62	1.95	23.4	14.5
QUENCH 2	17.5	16.40	36.00	2.48	40.30	1.45	0.96	0.74	0.89	0.86	2.20	26.1	16.5
QUENCH 3	14.5	22.80	53.40	2.34	15.70	1.65	1.31	0.78	1.20	0.28	2.34	21.6	13.7
QUENCH 4	13.1	23.90	53.00	2.25	14.70	1.81	1.57	0.81	1.18	0.27	2.22	20.6	12.6
PUSH 1	11.2	19.00	52.40	9.18	12.20	1.99	1.18	0.87	1.06	0.35	2.76	18.5	9.9
PUSH 2	18.0	15.20	47.60	3.61	27.70	1.67	1.07	0.86	0.89	0.55	3.13	24.7	16.6
PUSH 3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PUSH 4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PHEAT 1	25.3	11.50	41.90	13.40	25.70	1.87	0.96	0.80	0.71	0.79	3.64	26.3	25.1
PHEAT 2	64.1	6.69	74.40	1.22	14.10	1.06	0.95	0.51	0.64	0.22	11.12	65.0	64.0
PHEAT 3	29.8	11.50	38.30	7.03	37.00	1.52	0.84	0.67	0.85	0.93	3.33	26.5	30.7
PHEAT 4	14.0	23.20	44.70	1.83	24.80	1.64	1.24	0.75	1.22	0.44	1.93	23.0	12.9
BLEND 1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BLEND 2	43.9	8.75	47.20	34.60	4.49	1.93	0.78	0.57	0.38	0.75	5.39	47.0	42.9
BLEND 3	37.3	9.39	47.80	24.20	12.70	2.00	0.81	0.59	0.44	0.70	5.09	34.5	37.8
BLEND 4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
INTER 5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CBELT 1	96.8	5.36	89.80	0.96	1.27	0.94	0.89	0.42	0.14	0.05	16.75	93.5	97.1
CBELT 2	66.9	8.40	78.90	2.40	6.30	1.35	0.85	0.57	0.53	0.13	9.39	65.0	67.2
CBELT 3	57.5	7.64	80.70	2.37	5.23	1.28	0.83	0.53	0.53	0.12	10.56	57.7	57.5
CBELT 4	64.3	10.70	67.10	6.93	10.00	1.61	1.24	0.90	0.51	0.26	6.27	60.5	64.8
TDIST 1	88.0	8.74	81.90	3.20	2.31	1.16	1.37	0.49	0.27	0.09	9.37	79.3	88.5
TDIST 2	82.8	5.47	89.10	0.77	1.70	1.02	0.93	0.44	0.25	0.05	16.29	66.7	84.3
GAS 1	86.6	5.12	90.30	0.31	1.70	1.01	0.47	0.43	0.45	0.04	17.64	86.0	86.7
FAR 1	85.1	6.70	86.70	0.45	3.09	1.08	0.78	0.46	0.55	0.06	12.94	nd	nd
FAR 2	86.8	8.50	82.40	0.46	5.16	1.18	0.98	0.49	0.58	0.09	9.69	nd	nd
FAR 3	87.3	7.20	84.00	0.50	5.22	1.11	0.71	0.46	0.57	0.09	11.67	nd	nd
FAR 4	87.5	8.43	84.20	0.54	3.28	1.20	0.97	0.49	0.65	0.07	9.99	nd	nd
EXTERNAL 1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd: not determined

Table 4. Accuracy and precision obtained for trace element analysis in three reference soil samples by ICP-MS.

	<i>LGC6138</i>						<i>CRM026-050</i>			<i>San Joaquin</i>	
	V	Cr	Cu	Zn	As	Pb	Be	Co	Cd	Ni	Sb
SD_{Total}	4.81	6.38	14.3	12.1	4.08	26.4	1.47	0.52	0.30	0.28	0.68
SD_{Instr.}	1.13	1.84	1.54	9.35	0.60	7.36	0.35	0.26	0.06	0.26	0.07
SD_{SP}	4.67	6.10	14.2	7.6	4.03	25.3	1.43	0.45	0.30	0.09	0.68
% RSD	9.91	6.83	11.8	2.94	11.9	6.34	1.93	4.83	0.60	1.99	9.93
X_{aver.}	48.5	93.3	121	409	34.3	416	18.1	5.44	9.44	14.1	6.87
X_{cert}	54.6	99.3	132	456	34.5	490	18.0	6.77	11.7	14.4	7.90
Err (%)	11	6	8	10	<1	15	<1	20	20	2	13

SD_{Total}: Total Standard Deviation; SD_{Instr.}: Instrumental Standard Deviation; SD_{SP}: Standard Deviation for sample preparation; RSD: Relative Standard Deviation; X_{aver.}: Average value for measurements; X_{cert.}: Certified value; Err: Error

Table 5. Results, in $\mu\text{g g}^{-1}$, obtained in the analysis of trace metals in the O horizon samples (0-4 mm depth) from the coking battery.

Sample reference	As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Se	V
QUENCH 1	16.6	0.38	0.52	4.56	12.9	111	0.06	92.2	11.2	356	1.07	1.44	13.4
QUENCH 2	21.8	1.04	0.36	6.45	20.5	97	0.1	141	16.7	200	1.57	1.09	15.6
QUENCH 3	10.5	0.27	0.21	2.47	13.4	31.9	0.11	57.7	7.96	230	0.73	0.95	16.8
QUENCH 4	10.3	0.98	0.29	2.76	16.4	39.7	0.12	47.6	12.5	105	1.16	1.07	22.9
PUSH 1	5.7	0.99	0.37	4.84	11.3	46.7	0.19	45.4	15.2	64.8	1.14	1.37	19.5
PUSH 2	11.7	0.81	1.27	6.34	19.5	137	0.19	184	23.1	317	2.2	2.07	16.1
PUSH 3	18.1	0.51	1.75	6.86	25.4	264	1.33	244	28.6	334	4.13	2.41	17.2
PHEAT 1	10	0.43	0.53	4.4	18.1	123	0.33	222	25.2	349	2.55	1.03	14.7
PHEAT 2	34.5	0.38	0.47	3.54	41.3	88.9	0.8	174	28.4	169	2.17	0.51	18.4
PHEAT 3	19.5	0.53	1.53	8.15	32.6	497	0.83	326	40.2	548	2.32	0.87	17.5
PHEAT 4	20.4	0.65	0.56	3.73	50.5	176	0.09	72.7	13.7	125	1.61	1.44	56.9
BLEND 2	10.8	0.9	0.37	2.64	11	27.8	0.19	122	14.4	103	1.63	1.06	16.4
BLEND 3	13.7	0.6	0.49	4.62	17.2	50.9	0.27	199	21.6	437	2.12	0.96	18.7
CBELT 1	13.3	0.77	0.01	1.19	3.4	4.63	0.04	51.5	3.44	16.9	0.66	0.16	4.76
CBELT 2	14.1	0.78	0.49	3.58	16.4	32.5	0.21	197	18	171	2.3	0.86	19.6
CBELT 3	17.1	0.8	0.19	2.73	17.8	28.5	0.14	153	17.1	234	1.35	0.54	27.1
CBELT 4	25.4	1.82	0.37	4.01	18.9	37.2	0.2	257	23.4	181	2.17	0.76	26.9
TDIST 1	12.5	0.99	0.39	1.97	44.1	29	19.9	71.1	8.71	134	0.99	0.29	25.1
TDIST 2	9.93	0.61	0.16	1.32	12.4	15.9	1.25	53.6	5.39	44.1	0.81	0.31	9.12
GAS 1	8.74	0.29	0.24	0.99	12.7	10.4	0.14	73.1	3.43	47.1	0.64	0.28	16.04
FAR 1	14.7	0.88	0.31	3.35	9.6	13	0.17	99.1	6.54	30.2	0.62	0.32	23.5
FAR 2	24.5	1.3	0.27	4.69	14.3	14.8	0.14	130	9.19	34.1	0.78	0.36	32.7
FAR 3	24.8	1.23	0.34	7.62	13.7	20	0.1	325	10.2	46.4	0.81	0.28	41
FAR 4	15.1	0.76	0.24	3.28	13.3	15	0.19	111	7.67	31.3	0.9	0.35	26.9
Dutch Standards:	29-55	1.1-(30)	0.8-12	20-240	100-380	36-190	0.3-10		35-210	85-530	3.0-15	0.7-(100)	42-(250)
Optimum-Action*													
Soils	1-50	<5-40	0.02-10	1-40	5-1000	2-100	0.01-0.05	200-3000	5-500	2-100	0.2-10	0.1-2	20-500
Coal	0.5-80	0.1-15	0.1-3	0.5-30	0.5-60	0.5-50	0.02-1	5-300	0.5-50	2-80	0.05-10	0.2-1.4	2-100

* Ministerie-van-Volkshuisvesting, 2000. Directorate-General for Environmental Protection, Department of Soil Protection (Holland).

Table 6. Relationship between the trace element content and the levels of the organic particulate concentration determined from the O horizon samples of the soil in the studied area. Comparison of trace element concentrations with the values reported by Swaine (1990) for world coals.

	> 80 % vol.	80-50 % vol.	50-20% vol.	< 20 % vol.	World Coals
Co	2.47 - 8.15	4.62 - 6.86	2.64 - 4.40	0.99 - 7.62	0.5 - 30
Cr	11.3 - 50.5	17.2 - 25.4	11.0 - 41.3	3.4 - 44.1	0.5 - 60
Cu	31.9 - 497	50.9 - 264	27.8 - 127	4.63 - 37.2	0.5 - 50
Mn	45.4 - 326	122 - 244	122 - 222	51.5 - 325	5 - 300
Ni	7.96 - 40.2	21.6 - 28.6	14.4 - 28.4	3.43 - 23.4	0.5 - 50
Pb	64.8 - 548	317 - 417	103 - 349	16.9 - 234	2 - 80
V	13.4 - 56.9	16.1 - 18.7	14.7 - 27.1	4.76 - 41.0	2 - 100
Cd	0.21 - 1.53	0.49 - 1.75	0.19 - 0.53	0.01 - 0.39	0.2 - 10
Hg	0.06 - 0.83	0.19 - 1.33	0.14 - 0.80	0.04 - 1.25	0.02-1
Sb	0.73 - 2.32	2.12 - 4.13	1.35 - 2.55	0.62 - 2.17	0.5 - 2.5
Se	0.87 - 1.44	0.96 - 2.41	0.51 - 1.06	0.16 - 0.76	0.2 - 1.6
As	5.7 - 21.8	11.7 - 18.1	10.0 - 34.5	8.7 - 25.4	0.5 - 80
Be	0.27 - 1.40	0.51 - 0.81	0.38 - 0.90	0.29 - 1.82	0.1-15
Zn	73.0 - 555	296 - 899	255 - 1329	56.3 - 5461

Figure 1

Figure 2

Figure 3

Figure 4