

## Bioavailability of PAHs and PCBs in coal-containing soil samples from Svalbard



- Front page photo: Pyramiden, Svalbard.

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Bioavailability of PAHs and PCBs in coal-containing soil samples from Svalbard	
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<b>Summary</b>	
<p>In order to test the bioavailability of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) of soil from Pyramiden, Svalbard, an experimental study was conducted. Soil from different areas, representing different contaminant concentrations and coal content, was mixed with coal and water and kept cold (5 °C) for 51 days. Within each bucket of soil a passive samplers was embedded. The passive samplers absorb contaminants from the water phase (<math>C_{free}</math>), and concentrations of PAHs and PCBs in the passive samplers were used as a proxy for the bioavailable fraction. The results from the experiments shows that soil properties, such as total organic carbon (TOC), the binding of organic carbon and the concentrations of PAHs and PCBs were more important for the desorption/sorption processes than the experimental variables (coal and water added). Many of the soil samples had a high coal content as part of their "natural" properties. The desorption/sorption of PAHs and PCBs from these samples were generally lower than from samples with lower organic carbon content. Added coal had an impact on the bioavailable concentrations for some compounds. Even though soil properties had higher influence on the sorption processes of PAH and PCB, the addition of coal decreased the bioavailability in soil with initial low coal content. It is possible that adding more coal will increase the effect. A relatively low uptake in the passive samplers, despite high contaminant concentrations in soil, indicate that the contaminants are strongly bound, and that a moderate fraction is bioavailable under natural conditions. This means that the transport with water is relatively low. However, transport from land to sea with particles will still occur. Local coal might be a simple and cost-effective remediation measure for some of the present contaminants, but more research is needed in order to quantify the amount of coal that will give a significant effect for the different soils.</p>	
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# Preface

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The project presented in this report has been a collaboration between Akvaplan-niva (project leader), the Norwegian Institute for Water Research (NIVA) and Arctic and Antarctic Research Institute Analytical Laboratory (AARI), Barentsburg, Svalbard. The project has been funded by Svalbard Environmental Protection fund.

Tromsø 01.04.2019

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# 1 Sammendrag

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Undersøkelser utført av Norges Geologiske Undersøkelser (NGU) har vist at jorda i deler av Barentsburg og Pyramiden inneholder svært høye konsentrasjoner av polyklorete bifenyler (PCB). Undersøkelser utført av Akvaplan-niva har vist at forurensning på land har spredt seg til det marine miljø. Det ser imidlertid ut til at spredning fra land til sjø hovedsakelig har skjedd under flomhendelser, dvs. med partikler, og det er usikkert hvor mye som har blitt transportert oppløst i vann. Det er den oppløste fraksjonen som er tilgjengelig for opptak i planter og dyr (den biotilgjengelige fraksjonen). Biotilgjengelighet og spredning påvirkes i stor grad av lokale forhold (geologi, temperaturer, nedbør, vind, osv.), og det er derfor ikke alltid mulig å vurdere effekten av forurensning uten å gjennomføre stedsspesifikke undersøkelser. Svalbard har unike geologiske forhold som kan påvirke forurensningsdynamikken i enkelte områder. Kull, som finnes naturlig i berggrunnen flere steder, kan absorbere enkelte forurensningskomponenter og dermed redusere biotilgjengelighet.

For å teste hvordan biotilgjengelige polysykliske aromatiske hydrokarboner (PAH) og PCB er i jord fra Pyramiden på Svalbard, ble det utført en eksperimentell studie. Jord fra forskjellige områder, som representerer et spekter av forurensningskonsentrasjoner og kullinnhold, ble blandet med ulike mengder kull og vann. Deretter ble passive prøvetakere plassert i jord/kullblandingen og prøvene stod ved lav temperatur (5 °C) i 51 dager. De passive prøvetakere absorberer miljøgiftene PCB og PAH fra vannfasen (Cfree), og konsentrasjonene i passive prøvetakere kan derfor brukes som et mål for den biotilgjengelige fraksjonen.

Resultatene fra forsøkene viser at jordegenskaper, som innholdet av totalt organisk karbon (TOC), binding av organisk karbon (S1, S2, S3) og konsentrasjonene av PAH og PCB, var viktigere for utlekkings- og absorpsjons-prosessene enn de eksperimentelle variablene (tilsatt kull og vann). Mange av jordprøvene hadde allerede et høyt kullinnhold som en del av de naturlige egenskapene ved jord fra Pyramiden og utlekkings- og absorpsjons-prosessene av PAH og PCB fra disse prøvene var generelt lavere enn for prøver med lavere organisk karboninnhold (mindre kull). Tilført kull påvirket de biologisk tilgjengelige konsentrasjonene av noen forbindelser. Selv om jordegenskaper hadde større innflytelse på tilgjengelighet for opptak av PAH og PCB, reduserte tilsatt kull biologisk tilgjengelighet av PAH og PCB i jord med et opprinnelig lavt kullinnhold. Det er mulig at en økt effekt kan oppnås ved å øke mengden tilsatt kull.

Et moderat opptak i de passive prøvetakerne, til tross for høye forurensnings-konsentrasjoner i jord, indikerer at forurensningene er sterkt bundet til jorda og at en begrenset andel er tilgjengelig for opptak i planter og dyr under naturlige forhold. Dette betyr også at transporten med vann er lav. Imidlertid vil transport fra land til sjø med partikler fortsatt forekomme.

Konklusjon fra undersøkelsen er derfor at høye forurensningskonsentrasjoner i Pyramiden representerer en moderat risiko for organismer siden biotilgjengeligheten er lav. Lokalt kull kan være et enkelt og kostnadseffektivt "bindemiddel" for noe av den påviste forurensningen, men det er behov for mer forskning for å kvantifisere hvor store mengder som trengs for å oppnå en betydelig effekt for de forskjellige jordtypene.

## 2 Summary

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Studies carried out by the Geological Survey of Norway (NGU) have shown that the soil in parts of Barentsburg and Pyramiden contains very high concentrations of polychlorinated biphenyls (PCBs). Studies carried out by Akvaplan-niva has shown that pollution on land has spread to the marine environment. However, it seems that the dispersion from land to sea mainly has happened during flooding events, i.e. with particles, and it is uncertain whether pollution are transported dissolved in water. The dissolved fraction is the one available for uptake in plants and animals (bioavailable fraction). Bioavailability and dispersion are largely influenced by local conditions (geology, temperatures, precipitation, wind, etc.) and it is therefore not always possible to assess the effect of a pollution without conducting site-specific investigations. Svalbard has unique geological conditions that can affect contaminant dynamics in some areas. Coal, which occurs in the bedrock several places on the archipelago, can absorb certain contaminants and thus reduce bioavailability.

In order to test the bioavailability of polycyclic aromatic hydrocarbons (PAHs) and PCBs of soil from Pyramiden, Svalbard an experimental study was conducted. Soil from different areas, representing different contaminant concentrations and coal content, was mixed with coal and water and kept cold (5 °C) for 51 days. Within each bucket of soil a passive samplers was embedded in the mixture. The passive samplers absorb contaminants from the water phase ( $C_{free}$ ), and concentrations of PAHs and PCBs in the passive samplers were a proxy for the bioavailable fraction.

The results from the experiments shows that soil properties, such as total organic carbon (TOC), the binding of organic carbon (S1, S2, S3) and the concentrations of PAHs and PCBs were more important for the desorption/sorption processes than the experimental variables (coal and water added). Many of the soil samples had a high coal content as part of their "natural" properties. The desorption/sorption of PAHs and PCBs from these samples seemed to be generally lower than from samples with lower organic carbon content.

Added coal had an impact on the bioavailable concentrations for some compounds. Even though soil properties had higher influence on the sorption processes of PAH and PCB, the addition of coal decreased the bioavailability in soil with initial low coal content. It is possible that adding more coal will increase the effect.

A relatively low uptake in the passive samplers, despite high contaminant concentrations in soil, indicate that the contaminants are strongly bound to the soil, and that a low fraction is bioavailable under natural conditions. This means that the transport with water is relatively low. However, transport from land to sea with particles will still occur.

The conclusion is therefore that the high contaminant concentrations in Pyramiden represent a moderate risk to organisms since the bioavailability is low. Local coal might be a simple and cost-effective remediation measure for some of the present contaminants, but more research is needed in order to quantify the amount of coal that will give a significant effect for the different soils.

## 3 Introduction

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### 3.1 Background

The Arctic mainly receives pollutants via long-range transport from various source areas in the more temperate part of the globe (AMAP 2009). However, recent studies have shown that also small settlements in the Arctic, such as the mining settlements on Spitsbergen, can be important sources for both old pollutants (e.g. polychlorinated biphenyls (PCBs), dichlorodiphenyl trichloroethane (DDT)) and pollutants of emerging concern (e.g. per- and polyfluorinated alkylated substances (PFAS), phosphorous flame retardants (OPFRs) and new brominated flame retardants (nBFR)) (Jartun et al. 2009; Evenset et al. 2006; 2009; Ahrens et al. 2016; Olsson 2016; Carlsson et al. 2018). In some of the settlements on Svalbard, pollution mainly from former mining activities presents a challenge. In these areas, PCB is the pollutant of highest concern due to the quantity, potential toxicity and dispersion into the environment. Studies carried out by the Geological Survey of Norway (NGU) have shown that the soil in parts of Barentsburg and Pyramiden contains very high concentrations of PCB (Jartun et al. 2009). Calculations show that the soil in Pyramiden contains about 430 kg PCB<sub>7</sub>/ km<sup>2</sup>, the amount in soil in Barentsburg is estimated to be about 300 kg/km<sup>2</sup>, while soil from Longyearbyen had much lower PCB concentrations (estimated amount of 3.3 kg/km<sup>2</sup>) (Pedersen et al. 2011). Studies carried out by Akvaplan-niva has shown that pollution on land has spread to the marine environment (Evenset et al. 2006; 2009). However, it seems that the dispersion from land to sea mainly has happened during flooding events, i.e. with particles, and it is uncertain whether some of these contaminants has been transported dissolved in water. It is the dissolved fraction that is bioavailable. Studies of local biota, both on land (snow bunting, Warner et al. 2019) and in the sea (benthos and fish, Hop et al. 2001, Evenset & Christensen 2009; 2011) have shown that the local sources have caused elevated levels in organisms living in vicinity of the settlements.

During recent years, environmental managers on Svalbard (Governor of Svalbard) have initiated mitigation measures for sources of PCB pollution, but no remediation of contaminated soil or sediments have been carried out. However, there is a risk that pollution from local sources will spread to more remote areas and, in order to make good decisions about possible measures to limit dispersion and exposure, it is important to increase the knowledge about bioavailability and dispersion potential for the environmental contaminants.

Bioavailability and dispersion are largely influenced by local conditions (geology, temperatures, precipitation, wind, etc.) and it is therefore not always possible to assess the effect of a pollution without conducting site-specific investigations. Svalbard has unique geological conditions that can affect contaminant dynamics in some areas. Coal, which occurs in the bedrock several places on the archipelago, can absorb certain contaminants and thus reduce bioavailability (Ghosh et al. 2003; Cornelissen & Gustafsson 2005). Coal extraction has also led to some coal dust in the soil in the settlements where active mining is or was on-going (dust flux from intermediate storages for coal). Activated charcoal is often used to cover up contaminated sediments (Cornelissen et al. 2005), or applied in water treatment filters, as it has a large surface that binds certain pollutants. Activated charcoal would thus likely adsorb contaminants more efficiently than coal dust. However, coal/coal dust is however also expected to have some effect. If the pollutants are bound tightly to coal/coal dust, they will not be available for uptake in animals and the risk associated with leaving the polluted soil as it is will be lower than in areas without coal or coal dust to stabilise the target pollutants.

A common measure to prevent the spread of pollutants is removal of the most polluted soil. This will be a very costly job in Svalbard as the soil masses will have to be transported to a landfill approved for containing polluted soil on the mainland. An alternative measure may be cover combined with encapsulation (cloth or absorbent masses) thereby stabilising the pollutants. In this project, we investigated whether local coal masses can be used to stabilise the contaminated soil and hence provide an alternative method that prevents dispersion. Coal dust itself can be a source of pollution, but coal hydrocarbons are tightly bound in the coal and thus have a very low bioavailability. The results from the project will be very useful for environmental management in the assessment of site-specific remediation options in polluted areas in Svalbard.

## 3.2 Passive samplers

Different passive sampling devices, such as silicon rubbers or semipermeable membrane devices (SPMDs), are often used in studies of soil as alternatives to total chemical measures. Such samplers absorb bioavailable organic contaminants and can therefore offer potential as a biological surrogate in soil systems. In this study, silicon rubbers were used to test bioavailability of PAHs and PCBs.

## 3.3 Objective

The objective of this project was to investigate whether coal in the soil of Pyramiden (Figure 1) was sufficient to reduce the bioavailability of organic pollutants, as well as to investigate whether local coal masses can be used as a mitigating measure to reduce the dispersion and bioavailability of pollutants.



*Figure 1. Pyramiden with some of the old buildings and equipment used during mining activities. Photo: Anita Evenset, Akvaplan-niva.*

## 4 Materials and methods

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### 4.1 Fieldwork

The fieldwork was carried out in October 2017. The soil from Pyramiden was very dry so it was decided to transport soil samples to the laboratory in order to set up experiments that allowed sufficient exposure of the passive samplers, since water (fluid elements) is needed to ensure contact and uptake between soil and the passive samplers. Soil samples (ca. 10 kg each) were taken from 15 stations in Pyramiden. Previous studies, carried out by NGU, had shown that soil from Pyramiden contained a wide range of PCB-concentrations (Jartun et al. 2009). A visual survey of the area confirmed that various amounts of coal and coal dust were present in different areas. Thus, soil samples from Pyramiden were well suited for the studies of bioavailability.

The upper 4 – 5 cm of soil were collected using a shovel and transferred to the laboratory in polypropylene buckets. Stations were selected based on information from NGU. The intention was to cover a wide spectre of contaminant concentrations. The soil was frozen after sampling and kept frozen until initiation of experiments. Information about sampling stations is in Table 1 and photo-registration of selected sampling are shown in Figure 2.



Figure 2. Sampling stations in Pyramiden, October 2017. Upper left – station 854, upper right – station 847, lower left – station 825, lower right – station 73.

Table 1. Sampling stations for soil in Pyramiden, October 2017.

Station	Location	Description of soil samples	Position
P854	Close to barrels with waste oil in garage	Black top-soil. Oil, smell of oil.	N78.65811 E16.33040
P856	By brick building, concrete on building.	Sand, fine-grained. Black. Pieces of coal, no smell.	N78.65819 E16.33231
P847	At transformer house. Yellow and red brick house. Sample taken under porch.	Black sand. Pieces of coal.	N78.65728 E16.32572
P825	Inside the workshop (white) up in the hillside. Blue paint on a wall. Sample taken inside the workshop garage. Pipes around. Concrete floors cover most areas with some sand. Door / windows away, open for wind and weather	Sand. Some pebbles, no coal.	N78.65914 E16.31831
Ny 1	Inside buildings around / under tank facilities	Dust/plaster on floor	N78.66012 E16.30847
P943	Inside corrugated iron shed/tank area. Upgraded oil barrels stored in the shed (probably full)	Sand/greasy soil, reddish (under trafo). No coal	N78.66013 E16.30731
P942	About. 5 m from station 943, outside ca. 3 m from cable gate.	Sand. Brown.	N78.66015 E16.30727
P70	About. 30 m below tank facilities. A little vegetation. Steep slope	Sand. Brown. Pebbles.	N78.65978 E16.30796
Ny 2	At cable gate, close to tank facilities	Sand. Brown with wooden tiles. (from cable gate)	N78.65995 E16.30877
Ny 3	In small stream from the mountainside. Downstream white workshop and just below cable gate that goes up to mine.	Fine-grained, black sediment. Coal fragments and coal dust.	N78.65796 E16.31961
P 78	Inside building under the old trafo room, open so that water flows through.	Fine-grained sand. Grey. No visible coal.	N78.65833 E16.2019
P73	Under cable car	Dark brown soil. Dry. Kittiwakes nesting above. Some coal fragments.	N78.65920 E16.31969
P74	Below the machine room for the cable car, south of the cable car.	Fine-grained sand. Black. A lot of coal in area.	N78.65910 E16.32310
P866	Under transformer, below consulate, some vegetation.	Sand. Brown - gray, no visible coal	N78.65655 E16.34063
P53	In river.	Sand, fine-grained. Black, contained coal dust.	N78.65464 E16.34864

## 4.2 Experimental set-up

The idea behind this study was to use passive samplers to study bioavailability of contaminants in soil.

One kilo of thawed soil from each sample was mixed with different amounts of water and coal (Table 2) for investigations of the impact of coal on PCB and PAH bioavailability in the soil. One passive sampler was added to each bottle and they were left cold (5°C) and dark for 51 days. During this time, the bottles were regularly shaken (manually) to allow contact and exchange of compounds between the passive sampler and the water phase and the soil phase. Concentrations measured in the passive samplers ( $C_{\text{free}}$ ) are the fraction of PCBs and PAHs soluble from soil into water and can therefore be used as a proxy for the bioavailable concentrations.

Table 2. Overview of experimental setup.

Experiment no.	Station	Soil (g)	Coal added (g)	Water added (g)
4	P Ny 3	1000	50	1000
5	St 847	1000	25	750
7	St 847	1000	25	750
9	P866	1000	0	1000
10	P74	1000	0	500
11	P74	1000	50	1000
12	P825	1000	50	500
14	P825	1000	0	1000
15	P 78	1000	50	1000
16	P73	1000	0	1000
18	P73	1000	50	500
17	P943	1000	0	500
19	P943	1000	50	1000
21	P943	1000	50	500
24	Ny 1	1000	0	500
25	Ny 2	1000	0	1000
26	Ny 2	1000	50	250

### 4.3 Preparation of passive samplers

Passive samplers (0.5 mm thick altesil silicon rubbers; SRs) were spiked with performance reference compounds (PRCs) which are used to control the state of equilibrium between passive samplers and the matrix. The technique is based on uptake rate of target compounds into the passive sampler, which is calculated from the depuration rate of PRCs from the sampler. After exposure, the concentration of PRCs in thin the SRs was measured and used for calculations of the uptake rate as described in Booij et al. (2002). The sampling rate ( $R_s$ ) can be estimated when the weight of the sampler ( $m$ ) and the distribution coefficient ( $K_{pw}$ ) between SR and the matrix is known. From this, the freely dissolved water concentration ( $C_w$ ) of the target compounds can be estimated as follows:

$$C_w = \frac{n_{acc}}{K_{pw}m(1 - e^{\frac{-R_s t}{K_{pw}m}})}$$

$n_{acc}$  represents the accumulated mass of a target compound in the SR and  $t$  is the time of exposure.

## 4.4 Chemical analyses

### 4.4.1 TOC in soil samples

Total organic carbon content (TOC) was determined in dried and acidified soil using an IR 212 carbon analyser. Sediment was combusted in an oxygen atmosphere and any carbon present was converted to CO<sub>2</sub>. The sample gas flowed into a non-dispersive infrared (NDIR) detection cell. The NDIR measures the mass of CO<sub>2</sub> present. The mass was converted to percent carbon based on the dry sample weight. TOC-analyses were performed by Akvaplan-niva.

### 4.4.2 Rock eval pyrolysis

Rock eval pyrolysis was used to identify the type and maturity of organic matter in the soil. The analysis was carried out by Applied Petroleum Technology AS in Oslo. The soil samples were placed in a vessel and were progressively heated to 550°C in an inert atmosphere. The pyrolysis oven temperature program was as follows: for 3 min, the oven was kept isothermally at 300°C and the free hydrocarbons were volatilized and measured as the S1 peak (detected by FID). The temperature was then increased from 300° to 550°C (at 25°C/min). This is the phase of volatilization of the very heavy hydrocarbons compounds (>C40) as well as the cracking of nonvolatile organic matter. The hydrocarbons released from this thermal cracking were measured as the S2 peak (by FID). The temperature at which S2 reaches its maximum depends on the nature and maturity of the kerogen and is called *T*<sub>max</sub>. The CO<sub>2</sub> issued from kerogen cracking was trapped in the 300°-390°C range. The trap was heated, and CO<sub>2</sub> released and detected on a Thermal Conductivity Detector (TCD) during the cooling of the pyrolysis oven (S3 peak).

### 4.4.3 PCBs in soil samples

PCBs in soil samples were determined by AARI, Barentsburg. Stones, pebbles and large inclusions were removed from the soil prior to contaminant analyses. The soil was freeze-dried and 1-10 grams of sample were weighted before 30 mL of acetone and 100 µL of PCB #198 400 ng/ml in isooctane (internal standard) was added. Extraction was done with an ultra-sonic extractor for 5 minutes before the samples were centrifuged at 4000 rpm. Extraction was repeated with 30 ml of mixture acetone-hexane (1:1) and then with 30 ml of hexane. The extracts were combined and washed with 100 mL of 2% Na<sub>2</sub>SO<sub>4</sub> water solution in separating funnels for 5 minutes and thereafter dried with 5 g Na<sub>2</sub>SO<sub>4</sub>. The extracts were concentrated in a rotary evaporator to approximately 1 ml and cleaned by shaking with 1 mL of concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) a few times until the acid stays transparent. Thereafter 0.5 grams of silica gel impregnated with sulphuric acid was added and the mixture was left overnight. Then extract was washed with 2-3 ml of distilled water, then 2-3 mL of 1% NHCO<sub>3</sub> and twice with 2% Na<sub>2</sub>SO<sub>4</sub>. The extracts were once again dried with Na<sub>2</sub>SO<sub>4</sub> before transfer to GC vials, 10 µL of 1,2,3,4-tetrachloronaphthalene was added and the sample volume was reduced to exactly 1 mL.

Samples were analysed on gas chromatograph with electron capture detector Shimadzu GC-2010 Plus with Zebron ZB-Cl Pesticides-2 column film thickness 0.2 µm, id 0.255 mm, length 30 m. Hydrogen was used as carrier gas. The initial oven temperature was held at 75 °C for 1 min and then raised to 250 °C at a rate of 3.5 °C/min, held for 1 min, raised to 280 at 5 °C/min, and the final temperature was held for 2 min. Calibration was performed regularly using a

mixture of VWR analytical standards in the range 0.4-20 ng/mL. The detection limit was 0.1 ng/mL and precision was below 20% ( $\sigma$ ) for all measured compounds.

#### 4.4.4 PAHs in soil samples

PAHs in soil samples were determined by AARI, Barentsburg. 30 ml of methanol and 200-500  $\mu$ l of benzo[b]chryzene (internal standard) was added to 1-10 grams of the freeze-dried sample. Extraction was carried out with ultra-sonic extractor for 5 minutes and the sample was left overnight for extraction before being centrifuged at 4000 rpm. This extraction step was repeated twice with 30 ml of hexane for 10 min and then for 5 minutes. The extracts were combined and washed with 100 ml of 2% Na<sub>2</sub>SO<sub>4</sub> water solution in a separating funnel for 5 minutes and dried with 5 g of dry Na<sub>2</sub>SO<sub>4</sub>. The extracts were concentrated in a rotary evaporator to approximately 1 mL and cleaned on a silica column (sample was introduced to a column containing 4 grams of silica gel impregnated by 1.3% of water), then 10 ml of hexane was added, and PAHs were eluted by 30 mL of ethyl acetate (5% in hexane). The cleaned extract was concentrated by rotor evaporator to approximately 1 mL and then dried under a gentle stream of air. Exactly 1 mL of acetonitrile was added to dissolve residues, the sample was filtered through a syringe filter and injected to a Shimadzu HPLC 20 series equipped with a Supelcosil LC-PAH Column 5  $\mu$ m, id 15 cm, 4.6 mm connected to a diode array and fluorescent detector. Total flow of eluent was set to 1 mL/min at gradient mode, and the column oven temperature was 35 °C. The mobile phase was a gradient of water (A) - acetonitrile (B). Gradient program was following: 40% of B for 4 min, then raised to 100% at 42 min, held for 1 min and dropped back to 40% (B) in 1 min, held for 3 min.

The detection limit for all compounds was 1.2 ng/g. When the parallel samples were analysed the standard deviation did not exceed 30% for any compounds in most cases. However, for some samples (such as 53, Ny3, 825, 866) a significant interference of other organic compounds was detected, causing higher errors, up to 50%.

#### 4.4.5 PAHs and PCBs in passive samplers

Passive samplers were analysed by NIVA. The silicone sheets were rinsed with ultrapure water and dried with clean tissues. Extraction was done in 60 mL glass tubes filled with pentane for 24 h. The solvent was then transferred to clean glass tubes and evaporated under a gentle stream of nitrogen to <1 mL. Before determination of PCBs the extracts were cleaned with 2 mL concentrated sulphuric acid (95%) 2 times or more (repeated until no or little coloring of the extract could be observed).

Determination of PAHs, the PRCs, PCBs and hexachlorobenzene (HCB) was done on an Agilent 6890N Gas Chromatograph (GC) equipped with a 7683 Series Injector and a DB-5MS column (30 m \* 0.25 mm \* 0,25  $\mu$ m) coupled to a 5973 Network Mass Spectrometer operated in electron impact ionization SIM-mode. The flow of helium was set to 1.2 mL/min and the GC temperature program consisted of a step of 60°C (held for 2 min) prior to an increase to 250°C (at the rate of 7°C/min) and a final increase to 310° (at the rate of 15°C/min) which was held for 6 min. Temperatures of the transfer line, ion source and quadrupole were set to 280°C, 230°C and 150°C, respectively. The relative response of surrogate internal standards (biphenyl-D10, acenaphthylene-D8, dibenzothiophene-D10, benzo[a]anthracene-D12, perylene-D12, pyrene-D10, PCB-30, PCB-53 and PCB-204) and 7-point calibration curves was used for

quantification. PAHs and PRCs were determined in the same run, while PCBs were determined in a different run, both with a run time of 39.14 min.

As quality control, spiked silicon rubbers were analysed along with the samples. The relative standard deviation varied between 4-9% from the known spiked concentrations of PAHs, which is well within limits for acceptable results regarding robustness and accuracy of the analytical method. Blanks were analysed parallel with the samples. No issues with contamination during the handling of samples were detected, except for C2- and C3-naphthalenes and C2-phenantrenes in the field blank and PCB-101 in low levels (3 ng/g sampler) although leading to exclusion of PCB-101 in three of the samples due to low concentrations in those samples. These compounds are not part of the total evaluation. Limits of detection (LODs) varied between 0.04-5.4 ng/L for PAHs except naphthalenes which were found also in the field blank and the detection limits were adjusted according to this; blank concentrations plus 3x standard deviations of all blanks (LOD ranged between 37.3-4439 ng/L for naphthalenes). However, no naphthalenes were detected in the laboratory blanks. The LODs for PCBs were 0.03-0.1 ng/L.

## 4.5 Statistical analyses

Multivariate design and analysis can be used as a tool for assessing the relative importance of variables in a remediation design. Factorial designs are constructed to independently determine both the effects of each factor and interaction effects. This is achieved by simultaneously varying the factors and investigating all possible combinations of the levels of factors. Most commonly two-level designs are used, accordingly a two-level factorial design with k-factors contains  $2^k$  experiments. Each factor is investigated at two fixed levels, continuous variables have a low and high value, determined by the experimental domain and discrete variables have two alternatives (e.g. two types of soil). Two-level factorial designs of 4-7 factors entail conducting 32-128 experiments, however by assuming that interaction effects between three or more variables are low compared to the main effects, the number of experiments can be reduced by constructing designs that are fractions of factorial designs,  $1/2^p$  of a complete factorial design, resulting in a total of  $2^{k-p}$  experiments. In a fractional factorial design, the experiments are widely distributed to cover a maximum variation over the experimental domain. The fractional factorial designs are constructed in a way to control confounding of main and interaction effects. The resolution of a design describes the degree to which main effects are confounded with two-variable, three-variable and higher order interaction effects. In a Resolution V design, e.g. 24-2, main effects are confounded with four-variable effects and two-variable interaction effects are confounded with three-variable interaction effects. Supplementing a fractional factorial design with experiments in the center of the experimental domain provides an estimate of the experimental error variance as well as the possibility of assessing potential curvature of the response surface.

Due to the heterogeneous properties of the soils applied in the experiments, the soil type was considered a discrete variable in the experimental design. Along with the continuous variables, quantity of coal added and volume of water, this made a total of three experimental variables. For each fractional factorial designs, only two levels of the variables are investigated, i.e. for soils this means two types of soil can be included. Since 11 types of soil were investigated, the entire experimental design consisted of six 23-1 fractional designs (experiments 1-4, 8-27), supplemented with three experiments representing the center of the experimental domain (exp. 5-7) with one soil type.

Multivariate analysis provides tools for analysing large sets of data, which is done by reducing the dimensions making it easier to visualise and retrieve trends. Two such tools are principal

component analysis (PCA) and projections onto latent structures (PLS). In PCA, differences and similarities in the variation of data are identified by calculating principal components, which are mutually orthogonal vectors that represent independent and uncorrelated variance of the initial descriptors; accordingly, correlated descriptors are described by the same principal component. In PLS the quantitative relation between a descriptor matrix, X, and a response matrix, Y, is calculated. In sorption studies, a quantitative relation between experimental variables and desorbed/sorbed pollutants can be calculated. The model may subsequently be used to evaluate the comparative influence of experimental variables on the sorption process. Advantages of PLS include simultaneous modelling of several responses, coping with collinearity between variables, coping with noise in the X and Y matrices, coping with moderate amounts of missing data (<20%) and since it is based on projections, it is possible to have more variables than objects.

SimcaP11 Software was used for PCA and PLS analysis. Since values of variables and responses varied in magnitude, the data was logarithmically transformed, centered and scaled to unit variance. PCA was made of the initial soil and coal properties (grain size, TOC, Rock eval, pollutant concentrations) to visualise similarities/differences in the soil types used in the sorption experiments. Score plots were obtained by projection of the original data onto the calculated orthogonal principal component vectors. Sediments with similar variance in their characteristics were plotted close to each other. The influence of each original descriptor to the principal component is reflected in a loading plot. Descriptors which have a strong contribution to the variation depicted in the score plot are found far from the origin in the loading plot. Positively correlated descriptors are projected close to each other, while negatively correlated descriptors are projected opposite to each other with respect to the axis center.

To assess possible correlations between the experimental variables and the results of the experiment, PLS models were employed. The X-matrix consisted of the experimental variables and the soil properties. The Y-matrix consisted of the pollutant concentrations in the passive samplers (ng/L). Variable Importance in the Projection (VIP) values present the absolute importance of each parameter in the model with respect to its correlation to all the responses (Y) and to the projection (X). The VIP values are calculated for each X variable by summing the squares of the PLS loading weights, weighted by the amount of sum of squares explained in each model component. High VIP values (>1) represent high influence of the variable(s) in the model, and VIP values <0.5 indicate low influence of the variable(s) on the model.

To assess viability and stability of the calculated PCA and PLS models, correlation factors, R<sup>2</sup>X and R<sup>2</sup>Y (the fraction of the X- matrix and Y-matrix, respectively explained by the model) and predictive powers, Q<sup>2</sup> (an estimate of the reliability of the model calculated by cross-validation) were used. In order to obtain a high predictive power, R<sup>2</sup>Y should be high. A value of R<sup>2</sup>Y >0.9 is excellent, while a value above 0.5 is good. The difference between R<sup>2</sup>Y and Q<sup>2</sup> should be as low as possible and a difference larger than 0.2-0.3 may indicate outliers or the presence of irrelevant variables in the X block.

## 5 Results and discussion

### 5.1 Soil characteristics

Results from analyses of grain size, TOC and Rock eval pyrolysis are shown in Table 3. The grain size in the soil samples varied, and the fraction <63  $\mu\text{m}$  ranged from 2.40 – 37.4 % of the total soil. TOC-values ranged from 1.78 – 112 mg/g dry weight (dw). The highest TOC-concentrations were measured in sample Ny 3 and P 73. Both these stations also had high S2-values, indicating high content of non-volatile organic matter. This is probably due to the presence of coal, as both samples contained coal fragments.

*Table 3. Results from grain size- and TOC-analyses, as well as Rock eval pyrolysis. S1 = the amount of free hydrocarbons (gas and oil) in the sample. S2 = the amount of hydrocarbons generated through thermal cracking of non-volatile organic matter. S3 = the amount of CO<sub>2</sub> (in milligrams CO<sub>2</sub> per gram of rock) produced during pyrolysis of kerogen. Tmax = the temperature at which the maximum release of hydrocarbons from cracking of kerogen occurs during pyrolysis. HI = hydrogen index ( $HI = [100 \times S2]/TOC$ ). OI = oxygen index ( $OI = [100 \times S3]/TOC$ ).*

Sample	Grain size	TOC	S1	S2	S3	Tmax	HI	OI
Unit	% < 63 $\mu\text{m}$	mg/g dw	mg/g	mg/g	mg/g	$^{\circ}\text{C}$		
Ny3	37.4	88.2	0.82	34.79	1.42	440	394	16
P 847	22.0	35.2	0.44	7.81	1.57	435	222	45
P 866	24.1	18.0	0.11	1.53	2.28	437	85	127
P 74	16.4	11.1	0.25	4.22	0.67	444	380	60
P 825	22.8	13.9	0.62	4.93	4.41	427	355	317
P 78	6.90	21.2	2.25	6.38	0.67	441	301	32
P 73	15.8	73.9	6.58	96.52	1.97	442	1306	27
P 943	23.9	6.79	6.79	1.75	2.45	415	361	342
Ny 1	2.40	1.78	0.05	0.57	1.39	423	320	781
Ny 2	14.6	112	4.77	32.0	21.5	328	286	192

S1, which is an indication for free hydrocarbons (gas and oil) in the sample varied from 0.05 (Ny 1) to 6.79 mg/g. An S1 >1 mg/g may indicate that there is oil in the sample. This was the case for the following samples: P 78 (under old transformer room), P 73 (under cable car), P 943 (near tank area, under transformer) and Ny 2 (at cable gate, close to tank facilities), i.e. all in areas where oil spills are likely to have taken place.

## 5.2 PCB and PAH in soil samples

The results from soil analyses showed elevated levels of PCBs and PAHs in Pyramiden (Table 4). The  $\Sigma$ PAH16 and  $\Sigma$ PCB7 is classified according to the Norwegian Environmental Protection Agency's system for soil (TA 2553/2009). This system is developed mainly for urban areas, and is not adapted to non-urban areas and not for Svalbard, but in order to set the values into a context the system is used to visualise the data. Class 1 represents good environmental quality, while class 5 represents very poor environmental quality. As can be seen from the table, PCB7-levels vary from 19.8 (class 2) – 6987  $\mu\text{g}/\text{kg dw}$  (class 5). In NGUs study they documented PCB7-levels in Pyramiden that varied from 2  $\mu\text{g}/\text{kg dw}$  to 1290  $\text{mg}/\text{kg dw}$  (Jartun et al. 2009).

Table 4. Concentrations of PAHs and PCBs ( $\mu\text{g}/\text{kg dw}$ ) in soil samples from Pyramiden. Colour code (only for  $\Sigma$ PCB7 and  $\Sigma$ PAH 16) according to the Norwegian Environmental Agency's classification system for contaminated soil (TA 2553/2009). For explanation of colour see below table. LOD = level of detection. N.a. = not analysed (due to interference).

Compound	Ny 3	P847	P866	P74	P825	P78	P73	P943	P942	P854	Ny 1	Ny 2	Coal
% < 63 $\mu\text{m}$	37,4	22	24,1	16,4	22,8	6,9	15,8	23,9	24,6	21,1	2,4	14,6	
HCB	0,21	0,19	0,28	0,13	0,26	0,00	3,06	0,41	0,14	n.a.	0,14	1,32	0,33
PCB31	2,70	11,1	2,54	0,00	6,25	0,47	8,21	5,54	4,13	n.a.	0,25	32,6	0,79
PCB28	1,86	5,39	1,95	0,00	5,54	0,28	3,97	3,57	2,25	n.a.	0,10	33,9	0,53
PCB52	2,66	217	59,1	2,62	82,1	9,64	166	159	101	n.a.	5,05	572	9,39
PCB101	2,83	588	117	7,26	216	24	467	504	235	n.a.	14,2	1371	16,6
PCB118	4,70	863	198	11,2	395	34	603	597	322	n.a.	24,6	1910	25,0
PCB153	1,87	500	105	7,21	205	21	353	425	209	n.a.	13,1	1069	12,7
PCB138	2,90	813	162	9,73	292	30	109	748	320	n.a.	21,5	1734	20,1
PCB180	0,29	136	21,8	1,60	38,0	4,85	63,4	128	59,1	n.a.	2,71	264	2,15
$\Sigma$ PCB 7	19,8	3133	666	39,6	1240	124	1773	2570	1253	n.a.	81,6	6987	87,2
fluorene	95,0	36,0	56,0	18,5	36,9	25,7	301	32,7	5,23	257	2,16	1722	581
phenanthrene	2110	825	508	386	594	586	4545	248	90	2292	23	20444	6342
fluoranthene	157	185	436	27	206	121	854	338	57	485	24	34825	456
benzo[a]anthracene	113	114	194	30,7	104	45,5	458	178	31,0	0,00	11,1	17537	534
chrysene	281	131	243	37,5	95,3	93,9	1028	153	43,7	0,00	18,0	18011	1109
benzo[b]fluorantene	169	149	256	13,1	76,8	68,2	857	218	56,2	175	15,0	18040	815
benzo[k]fluorantene	30,2	52,9	114	3,64	32,7	24,3	384	101	23,8	46,0	7,36	9004	112
benzo[a]pyrene	52,5	76,2	193	6,07	38,6	41,9	638	197	42,7	90,6	10,2	17003	277
dibenzo[a,h]-anthracene	6,99	5,16	15,7	0,00	6,12	3,23	47,3	13,6	3,00	17,6	0,00	1440	83,3
benzo[g,h,i]-perylene	232	147	191	28,7	79,3	101	1347	247	67,3	240	15,5	13651	1197
naphthalene	3026	834	205	624	329	756	4553	104	120	2032	22,1	660	5995
acenaphthene	9,60	10,08	42,4	2,26	4,93	4,60	63,8	8,14	1,25	18,5	0,00	1141	40,3
anthracene	13,0	15,2	45,7	1,57	22,4	9,19	172	42,6	7,30	22,2	2,05	3307	21,3
pyrene	257	202	336	45,6	189	109	1400	306	58,2	547	21,3	20320	498
indeno[1,2,3-cd]pyrene	38,5	66,8	183	5,46	30,8	20,5	561	259	49,5	101	14,6	14954	197
acenaphthylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	109	<LOD
$\Sigma$ PAH 16	6590	2851	3019	1230	1846	2010	17209	2444	656	6 323	186	192 169	18 258

Class 1 - Very good	Class 2 - Good	Class 3 - Moderate	Class 4 - Bad	Class 5 - Very bad
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$\Sigma$ PAH16 varied from 186 (class 1) – 192 169  $\mu\text{g}/\text{kg dw}$  (class 5). The highest levels of both PCB and PAH was measured in a sample (Ny 2) taken under the cable gate, close to tank facilities.

### 5.3 PCB and PAH in passive samplers

Passive samplers were exposed in each experiment and the absorbed PAHs and PCBs in these samplers represent  $C_{\text{free}}$ , i.e. the concentration of these contaminants dissolved in the water. The uptake of PCBs was relatively low, so calculated water concentrations varied from  $< \text{LOD}$  – 123  $\text{ng}/\text{L}$  (Table 5). The highest concentration was measured in the experiments with soil from station Ny 2, the station with highest PCB-levels in soil.

For PAHs the calculated concentration of PAH16 in water varied from 1 – 3 906  $\text{ng}/\text{L}$  (Table 5). Also for PAHs, the highest concentration was measured in the experiments with soil from Ny 2. This was not unexpected as PAH-levels in Ny 2 soil were approximately 10x higher than in the other soil samples.

High concentrations of other hydrocarbons sometimes interfered with the chemical analyses both in soil and in the passive samplers, therefore some values are missing in Table 4 and Table 5.

Table 5.  $C_{free}$  of PAHs and PCBs (ng/L) in soil samples from Pyramiden, where water and coal were added in different experiments. LOD = level of detection. N.a. = not analysed (due to interference).

Sample	P Ny3	St 847	St 847	P866	P74	P74	P825	P825	P73	P943	P73	P943	P943	Ny 1	Ny 2	Ny 2
Coal (g)	50	25	25	0	0	50	50	0	0	0	50	50	50	0	0	50
Water (g)	1000	750	750	1000	500	1000	500	1000	1000	500	500	1000	500	500	1000	250
<b>HCB</b>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.03	0.03	0.03	0.04	0.1	0.03	<LOD	<LOD	0.1	1
<b>PCB 31+28</b>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.2	0.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1	3
<b>PCB 52</b>	<LOD	1	1	2	<LOD	<LOD	4	4	1	6	1	4	<LOD	<LOD	10	39
<b>PCB 101</b>	<LOD	0.4	1	2	<LOD	<LOD	4	3	0.5	5	1	4	<LOD	<LOD	8	28
<b>PCB 118</b>	<LOD	0.4	1	1	<LOD	<LOD	3	3	0.2	3	1	3	<LOD	<LOD	7	24
<b>PCB 153</b>	<LOD	0.4	1	1	<LOD	<LOD	2	1	0.3	1	1	3	<LOD	<LOD	4	14
<b>PCB 138</b>	<LOD	0.4	1	1	<LOD	<LOD	2	2	0.3	2	1	2	<LOD	<LOD	4	14
<b>PCB 180</b>	<LOD	0.1	0.1	0.1	<LOD	<LOD	0.1	0.1	0.02	0.1	0.04	0.2	<LOD	<LOD	0.3	1
<b>∑PCB7 *</b>	<LOD	2	5	7	<LOD	<LOD	16	13	2	17	4	17	<LOD	<LOD	34	123
<b>Naphtalene</b>	86		<LOD	<LOD	<LOD	<LOD	97	145	238	118	153	122	<LOD	<LOD	1137	<LOD
<b>C1-Naphtalenes</b>	76	39	51	n.a.	35	34	445	425	587	193	416	481	<LOD	109	572	223
<b>C2-Naphtalenes</b>	267	225	226	n.a.	<LOD	<LOD	1 756	2 360	1 205	311	1 066	1 105	412	356	1318	683
<b>C3-Naphtalenes</b>	<LOD	<LOD	<LOD	n.a.	<LOD	<LOD	13 583	18 323	<LOD	<LOD	3 784	<LOD	<LOD	<LOD	<LOD	<LOD
<b>Acenaphthylene</b>	5	<LOD	<LOD	n.a.	<LOD	<LOD	3	2	2	21	2	18	<LOD	<LOD	347	22
<b>Acenaphthene</b>	<LOD	<LOD	<LOD	n.a.	<LOD	<LOD	5	6	6	9	4	4	<LOD	<LOD	258	225
<b>Fluorene</b>	0.4	0.2	<LOD	n.a.	<LOD	<LOD	3	4	3	10	2	<LOD	<LOD	1	383	60
<b>Phenantrene</b>	2	1	1	n.a.	1	1	46	79	14	32	11	19	2	11	508	115
<b>Antracene</b>	0.4	0.1	0.1	n.a.	<LOD	<LOD	1	2	2	8	2	3	<LOD	1	446	24
<b>Fluoranthene</b>	1.2	0.3	0.2	n.a.	0.05	<LOD	11	11	2	21	2	13	0.1	11	334	58
<b>Pyrene</b>	1.0	0.2	0.2	n.a.	0.05	0.1	11	11	9	14	10	10	0.1	8	262	53
<b>Benzo(a)anthracene</b>	0.3	0.0	0.1	n.a.	0.01	0.01	0.3	0.2	0.1	0.6	0.1	0.4	0.02	1	56	48
<b>Chrysene</b>	0.4	0.1	0.1	n.a.	0.02	0.02	1.0	0.6	2.8	0.7	3.5	0.7	0.04	1	77	99
<b>Benzo(b,j)fluoranthene</b>	0.5	0.1	0.1	n.a.	0.02	0.02	0.3	0.3	0.2	0.5	0.5	0.3	0.04	1	35	54
<b>Benzo(k)fluoranthene</b>	0.1	0.02	0.03	n.a.	0.002	<LOD	0.1	0.1	0.02	0.1	0.1	0.1	<LOD	0.2	14	15

<i>Benzo(e)pyrene</i>	<LOD	0.1	0.2	n.a.	0.05	0.1	0.4	0.4	0.6	0.4	1	0.3	0.1	1	16	24
<i>Benzo(a)pyrene</i>	0.3	0.04	0.1	n.a.	0.01	0.01	0.1	0.1	0.1	0.2	0.2	0.1	0.01	<LOD	22	20
<i>Perylene</i>	0.1	0.01	0.01	n.a.	0.01	<LOD	0.04	0.04	0.2	0.1	0.3	0.1	0.01	<LOD	5	5
<i>Indeno(1.2.3-cd)pyrene</i>	0.2	0.04	0.1	n.a.	<LOD	<LOD	0.04	0.05	0.1	0.1	0.1	0.1	<LOD	<LOD	11	13
<i>Dibenz(ac/ah)anthracene</i>	0.1	0.01	0.02	n.a.	<LOD	<LOD	0.02	0.01	0.03	0.02	0.1	0.02	<LOD	<LOD	3	4
<i>Benzo(ghi)perylene</i>	0.4	0.1	0.2	n.a.	0.05	0.1	0.1	0.1	0.2	0.1	0.4	0.1	0.1	<LOD	11	12
<b><math>\Sigma PAH_{16}</math></b>	<b>98</b>	<b>2</b>	<b>2</b>	<b>n.a.</b>	<b>1</b>	<b>1</b>	<b>178</b>	<b>262</b>	<b>281</b>	<b>235</b>	<b>191</b>	<b>191</b>	<b>3</b>	<b>36</b>	<b>3 906</b>	<b>822</b>

## 5.4 Model evaluation

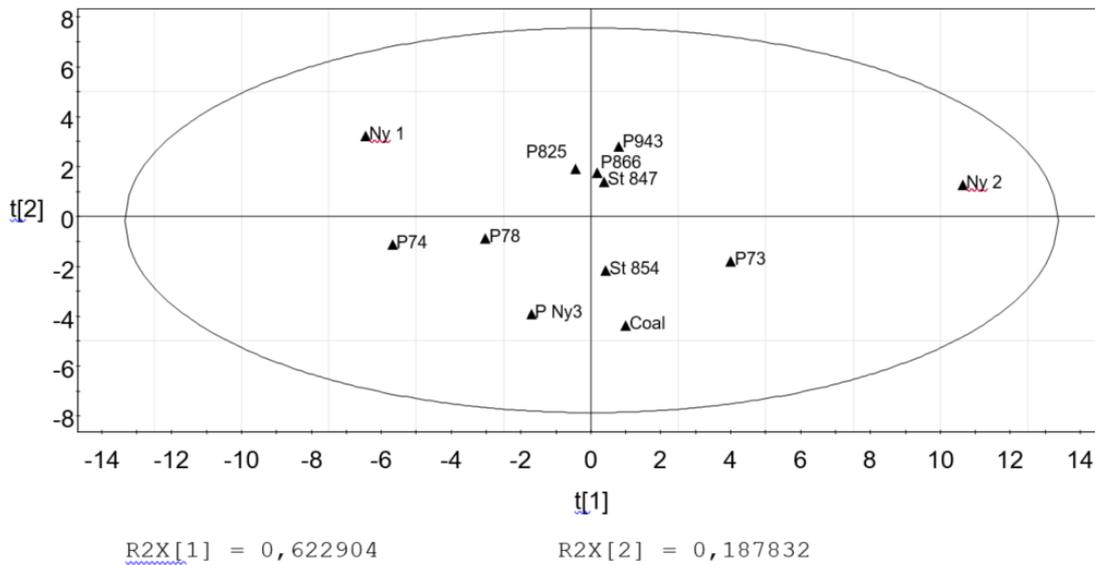
### 5.4.1 PCA-analyses

The PCA-analyses was run to explore variability in soil samples and the coal used in the sorption experiments (Figure 3). The PCA-model included all analysed parameters: Rock eval analysis, grain size, PCB and PAH concentrations. Due to the high percentage of variance explained by the model (81%), the model is considered good. The model is further validated to be stable as the Q2 (53%) is moderate.

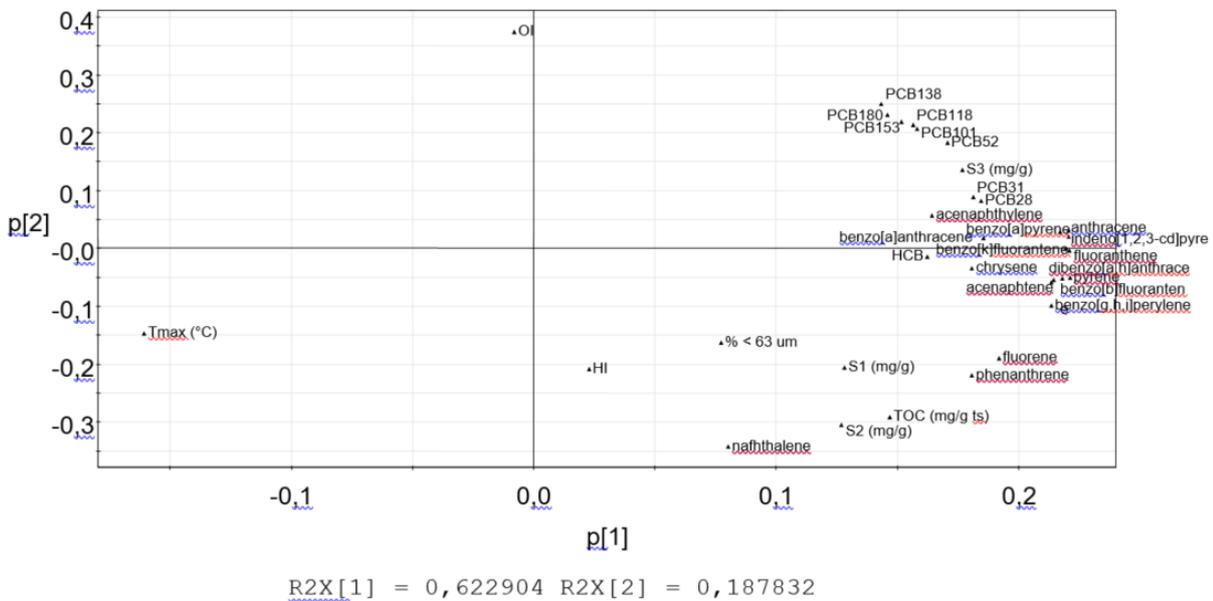
The soil types located close in the scores plot (Figure 3) have similar variance in their properties. The clustering of P943, P825, P866 and P847 indicates that these soil samples have similar properties. Apart from these four samples, there is a good spread of the soils in the scores plot, indicating that the soil of Pyramiden have a wide range in their properties.

In the loading plot, parameters with a high influence on the location of the soil types in the scores plot are located furthest from the origin (0, 0). PAH-components have high influence on the first component (t1 axis in scores plot) while oxygen index (OI) and naphthalene have highest influence on the second component (t2 axis in scores plot), albeit with opposite numerical influence (Figure 3).

Parameters located close to one another are likely correlated; i.e. the clustering of PCB-congeners indicate that PCB-congeners are correlated and that most PAH-components are correlated. S1, S2 and TOC are correlated. S3 is correlated to TOC in the first component, but not in the second component (18%), indicating that soils with a high TOC value do not necessarily have a high S3 value.



SIMCA-P 11 - 25.03.2019 01:58:47



SIMCA-P 11 - 25.03.2019 02:18:15

Figure 3. PCA scores (upper) and loading (lower) plots. The PCA model explains 81% of the variance in the dataset. The first component (first axis,  $t_1$ ) explains 62% of the variance in the dataset ( $R2X_1$  below the figure). The second component (second axis  $t_2$ ) explains 19% of the variance in the dataset ( $R2X_2$  below the figure).  $Q_2$  is 53% in the model –  $Q_2$  is a measure of the reliability of the model, determined by cross validation. Due to the high percentage of data variance explained by the model (81%), the model is good, and the fairly high  $Q_2$  indicates a relative stable model. ( $Q_2$  should be as close to  $R2X$  as possible, a model is considered stable if  $Q_2$  is <20% points below  $R2X$ , in this case 61%). The  $Q_2$  value in this model is a bit lower, but still indicates a fairly stable model.

### 5.4.2 PLS models

In order to evaluate the influence of experimental variables (soil type, water and coal) on the availability of PAH and PCB in the sorption experiments, PLS models were calculated.

In the PCA score plot, soils P825 and P943 were clustered, indicating similar soil properties. A PLS model was calculated to evaluate whether the influence of experimental variables on the sorption of pollutants was similar for the two soils. The PLS model included the experimental variables and numerical value for each soil (-1/1) as the X matrix and the  $C_{\text{free}}$  concentrations of PAH and PCB measured using passive samplers in the Y-matrix. The model had a low  $R^2Y$  (43%) and a low  $Q^2$  (<0) indicating an unstable model. VIP values showed that soil type was the most important variable. Along with the weak model, this indicates that the concentration of PAHs and PCBs in the passive samplers differed according to soil type. Despite being clustered in the PCA plot, soils P825 and P943 have different sorption capacities.

Since the type of soil affects the availability of PAH and PCB in the experiments, the soil properties were included as part of the X matrix in the next set of PLS models. By applying the soil properties instead of numerical values for each soil type, it was possible to include all experiments in the PLS models. (When applying numerical values for soil type, it is only possible to include two soil types per PLS model, since the experimental design was based on 2 level fractional factorial designs). A total of 30 PLS models were calculated, the first one included all the  $C_{\text{free}}$  concentrations of PAH and PCB calculated from the passive samplers. For the other 29 models, the Y-matrix only included one of each of the 29 analysed PAH/PCB components.

$R^2X$  is a measure of the fraction of the X-variables (experimental variables, soil characteristics) explained by the model. This is an indication of how well the experiments were designed. A value close to 1 means that the experimental design was excellent. This can be hard to accomplish with heterogeneous soils as it may be difficult to achieve a good variance in all of the soil characteristics. The PCA model of the soil properties however indicated a good variance for the soils used in the experiments in this study.

$R^2Y$  is a measure of the fraction of the variance in the responses that are explained by the model (here  $C_{\text{free}}$  pollutant concentrations measured by passive samplers). Ideally, this should be close to 1; however PLS models based on remediation studies seldom get close to 1. Anything above 50% is considered a good model.

$Q^2$  is a measure of how reliable the model is, determined by cross-validation.  $Q^2$  should be as close to  $R^2Y$  as possible. If it is anywhere below 20% points from  $R^2Y$  it is considered stable. If it is lower, the model can still be used for interpretation, however with some caution as to the stability of the model.

$R^2X$ ,  $R^2Y$  and  $Q^2$  for all of the models are shown in Table 6.

Table 6. R2X, R2Y and Q2 for the PLS-models.

	R2X	R2Y	Q2	Comment
<b>Total model</b>	0,71	0,66	0,42	Good, stable model
HCB	0,63	0,70	0,53	Good, stable model
PCB31+28	0,71	0,88	0,68	Good, stable model
PCB52	0,63	0,60	0,55	Good, stable model
PCB101	0,63	0,60	0,55	Good, stable model
PCB118	0,63	0,59	0,54	Good, stable model
PCB153	0,63	0,61	0,56	Good, stable model
PCB138	0,63	0,61	0,57	Good, stable model
PCB180	0,63	0,59	0,53	Good, stable model
Naftalen				No model
C1-Naphtalenes	0,64	0,32	0,24	Poor model
C2-Naphtalenes	0,63	0,38	0,27	Poor model
C3-Naphtalenes				No model
Acenaphtylene	0,86	0,82	0,54	Good, somewhat unstable model
Acenaphtene	0,72	0,92	0,81	Good, stable model
Fluorene	0,72	0,85	0,62	Good, stable model
Phenantrene	0,85	0,84	0,59	Good, somewhat unstable model
Antracene	0,73	0,81	0,59	Good, somewhat unstable model
Fluorantene	0,63	0,44	0,32	Poor model
Pyrene	0,63	0,50	0,39	Good, stable model
Benzo(a)anthracene	0,74	0,80	0,54	Good, somewhat unstable model
Chrysene	0,64	0,67	0,58	Good, stable model
Benzo(b,j)fluoranthene	0,72	0,84	0,56	Good, somewhat unstable model
Benzo(k)fluoranthene	0,73	0,87	0,66	Good, stable model
Benzo(e)pyrene	0,90	0,93	0,69	Good, somewhat unstable model
Benzo(a)pyrene	0,72	0,92	0,77	Good, stable model
Perylene	0,75	0,92	0,82	Good, stable model
Indeno(1,2,3-cd)pyrene	0,72	0,97	0,89	Good, stable model
Dibenzo(ac/ah)anthracene	0,87	0,97	0,88	Good, stable model
Benzo(ghi)perylene	0,87	0,99	0,97	Good, stable model

Most of the PLS models were good and stable. Three of the individual PLS models were poor and six of the individual PLS models were good, but unstable. Despite this, these models have been included in the evaluation of variable importance. Caution is advised when scrutinizing results of these models, they provide indications of variable importance and should be compared with models of similar pollutant properties for validation.

For an assessment of which variables are important for the sorption of pollutants desorbed from the soil, variable importance in the projection values have been used (Table 7). VIP values >1 have the highest influence on the models, VIP values 0,5-1 have moderate influence on the model and VIP values < 0,5 have a low influence on the model.

The PLS models that includes all PAH and PCB concentrations in the water (total model) has low VIP values of the experimental variables (coal and water added). The soil properties related to TOC and how carbon is bound in the soil (S1, S2, S3 and Tmax) along with the initial pollutant soil concentrations are more important for the desorption/sorption processes of PAH/PCB in the soils. The higher influence of S3 and Tmax compared to the moderate effect of TOC, S1 and S2 is likely related to the variance in the dataset. Ny 2 has the highest level of S3 and the lowest Tmax, and at the same time the highest concentrations of PAH and PCB in the C<sub>free</sub>. In the model, this result in higher VIP values for S3 and Tmax than TOC, S1 and S2. It is important to note that variables with a low influence on the model can still affect the

process, other variables are just more important. Adding coal can potentially still affect the sorption/desorption processes, the type of soil is however more important for the availability of the pollutants.

Table 7. VIP values for the total model assessing sorption of pollutants desorbed from the soil. Values >1 are highlighted in bold, values < 0.5 are “downlighted” in grey.

<b>Total model</b>	
<b>Experimental variables</b>	
Coal (g) added	0,17
Water (mL) added	0,30
<b>Soil characteristics</b>	
% < 63 um	0,09
TOC (mg/g ts)	0,71
S1 (mg/g)	0,68
S2 (mg/g)	0,54
S3 (mg/g)	<b>1,34</b>
Tmax (°C)	<b>1,26</b>
HI	0,08
OI	0,42
<b>Pollutant concentrations</b>	
HCB	0,86
acenaphtene	<b>1,19</b>
acenaphthylene	<b>1,24</b>
anthracene	<b>1,27</b>
benzo[a]anthracene	<b>1,26</b>
benzo[a]pyrene	<b>1,23</b>
benzo[b]fluorantene	<b>1,23</b>
benzo[g,h,i]perylene	<b>1,17</b>
benzo[k]fluorantene	<b>1,25</b>
chrysene	<b>1,21</b>
dibenzo[a,h]anthracene	<b>1,28</b>
fluoranthene	<b>1,29</b>
fluorene	<b>1,09</b>
indeno[1,2,3-cd]pyrene	<b>1,22</b>
nafhtalene	0,14
phenanthrene	0,95
pyrene	<b>1,23</b>
PCB28	<b>1,08</b>
PCB31	<b>1,02</b>
PCB52	0,98
PCB101	0,93
PCB118	0,94
PCB138	0,88
PCB153	0,91
PCB180	0,87

In order to assess similarities/differences in variable importance for each pollutant, VIP values for each of the individual models were calculated and are provided in Appendix 1. In general, the pollutant concentration in the soil, the TOC and binding of carbon (S1, S2, S3) were more important for the desorption/sorption processes than the experimental variables (coal and water added). However, the addition of coal still has an influence on the concentrations of some pollutants in the passive samplers, depending on the pollutant and type of soil. To illustrate the difference in the influence of added coal and water, contour plots of selected pollutants are

given in Figure 4. The white boxes in the contour plots are concentration of the given pollutant (the concentration follows the contour line where the white box is placed in the figure), as function of added coal (x-axis) and water (y-axis). The contour plots in Figure 4 are based on average values of soil properties (grain size, Rock eval, TOC, PAH and PCB concentrations) in the experiments and can be adjusted to a specific soil, e.g. the properties of Ny2, P943, etc. if the purpose is to study one specific soil. This will adjust the concentrations in the white boxes of the contour plots, the trend in concentration increase/decrease as function of added coal and water will however be the same.

For benzo(a)pyrene and PCB28-31, the contour plots illustrate that the addition of coal does not influence the concentrations in the passive samplers, whereas increasing the amount of water in the experiments decreases the pollutant concentration. For naphthalene, acenaftylene and anthracene, addition of coal reduces the concentration in the passive samplers, indicating that coal may retard mobilisation of these three pollutants.

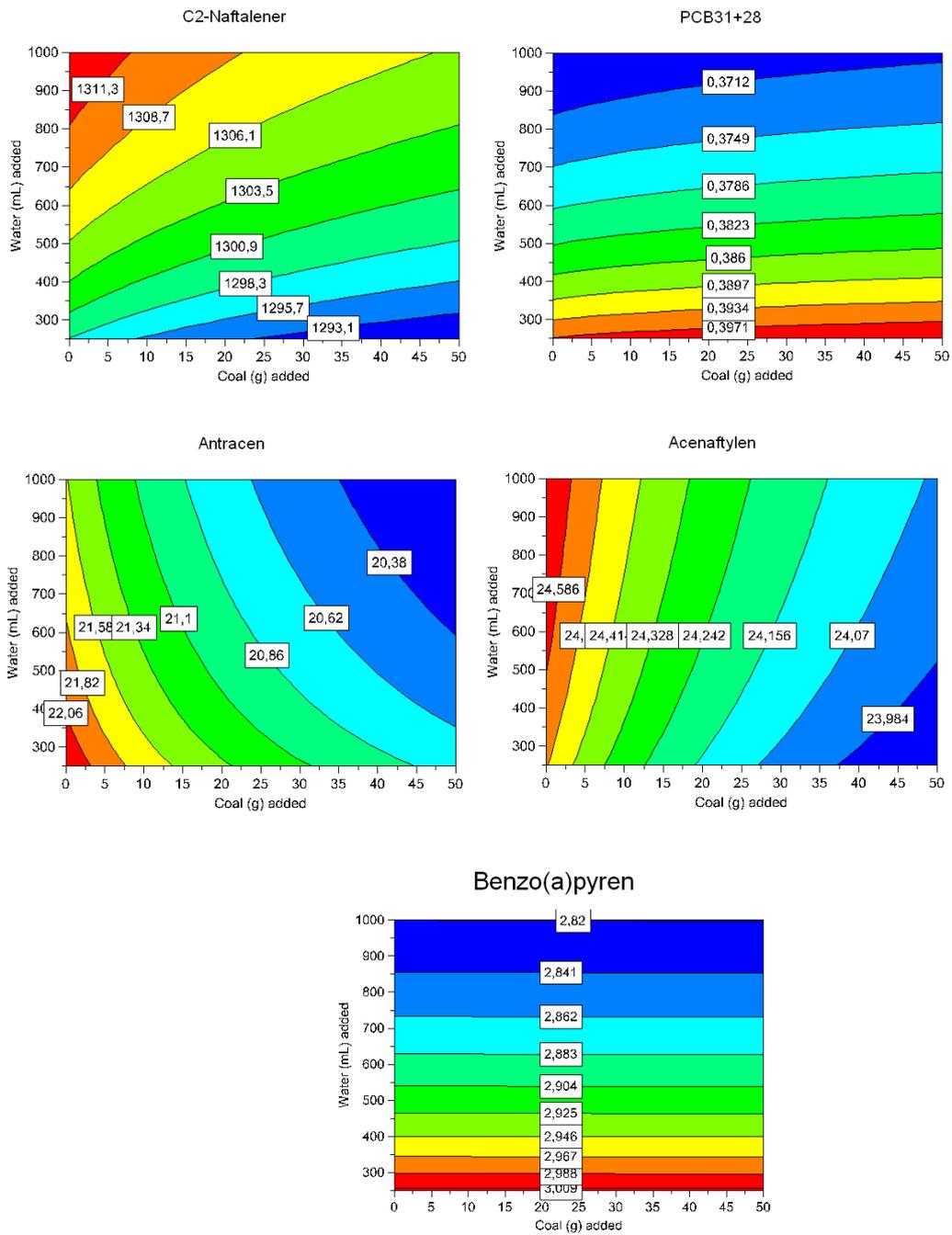


Figure 4. Contour-plots showing concentration in the passive samplers as function of added water and coal.

## 6 Conclusions

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The results from the experiments performed in the present project shows that soil properties, such as TOC, the binding of organic carbon (S1, S2, S3) and the concentrations of PAHs and PCBs were more important for the desorption/sorption processes than the experimental variables (coal and water added). Many of the soil samples had a high coal content (reflected in high S2, S3-values) as part of the natural properties and the desorption/sorption of PAH and PCB from these samples seemed to be generally lower than samples with lower organic carbon content.

Added coal had an impact on the bioavailable concentrations of some compounds. Even though soil properties had higher influence on the sorption processes of PAH and PCB, the addition of coal decreased the bioavailability in soil with an initially low coal content (P943). It is possible that adding more coal will decrease the bioavailability of the PAH and PACB contaminants.

A moderate uptake in the passive samplers, despite high contaminant concentrations in soil, indicate that the contaminants are strongly bound to the soil, and that a low fraction is bioavailable under natural conditions. This means that the transport with water is relatively low. However, transport from land to sea with particles will still occur.

The conclusion from the present study is therefore that the high contaminant concentrations in Pyramiden represent a moderate risk to organisms since the bioavailability is relatively low. Local coal can be a simple and cost-effective remediation measure for some of the present contaminants, but some more research is needed in order to quantify the different amounts that will give a significant effect for different soils.

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## Appendix 1 – VIP values for PLS-models

	HCB	PCB31+28	PCB52	PCB101	PCB118	PCB153	PCB138	PCB180
<b>Experimental variables</b>								
Coal (g) added	0,16	0,13	0,11	0,09	0,08	0,02	0,07	0,10
Water (mL) added	0,75	0,85	0,20	0,22	0,22	0,18	0,18	0,39
<b>Soil characteristics</b>								
% < 63 um	0,02	0,36	0,16	0,12	0,15	0,20	0,18	0,04
TOC (mg/g ts)	0,76	0,76	0,62	0,60	0,59	0,65	0,64	0,54
S1 (mg/g)	0,88	0,65	0,71	0,74	0,70	0,68	0,70	0,63
S2 (mg/g)	0,71	0,59	0,39	0,38	0,34	0,41	0,41	0,21
S3 (mg/g)	<b>1,23</b>	<b>1,49</b>	<b>1,25</b>	<b>1,26</b>	<b>1,30</b>	<b>1,24</b>	<b>1,24</b>	<b>1,36</b>
Tmax (°C)	<b>1,23</b>	<b>1,56</b>	0,91	0,93	0,97	0,92	0,91	<b>1,20</b>
HI	0,27	0,39	0,24	0,21	0,28	0,26	0,23	0,49
OI	0,25	0,64	0,40	0,43	0,48	0,36	0,37	0,58
<b>Pollutant concentrations</b>								
HCB	<b>1,00</b>	0,74	0,76	0,77	0,70	0,74	0,76	0,52
acenaphtene	<b>1,20</b>	<b>1,17</b>	<b>1,05</b>	<b>1,05</b>	<b>1,03</b>	<b>1,05</b>	<b>1,05</b>	<b>1,07</b>
acenaphthylene	<b>1,23</b>	<b>1,60</b>	0,84	0,85	0,88	0,85	0,85	<b>1,11</b>
anthracene	<b>1,25</b>	<b>1,15</b>	<b>1,20</b>	<b>1,21</b>	<b>1,20</b>	<b>1,20</b>	<b>1,20</b>	<b>1,19</b>
benzo[a]anthracene	<b>1,28</b>	<b>1,27</b>	<b>1,13</b>	<b>1,13</b>	<b>1,13</b>	<b>1,13</b>	<b>1,13</b>	<b>1,20</b>
benzo[a]pyrene	<b>1,23</b>	<b>1,12</b>	<b>1,13</b>	<b>1,14</b>	<b>1,12</b>	<b>1,13</b>	<b>1,13</b>	<b>1,15</b>
benzo[b]fluorantene	<b>1,22</b>	<b>1,14</b>	<b>1,11</b>	<b>1,12</b>	<b>1,10</b>	<b>1,12</b>	<b>1,12</b>	<b>1,13</b>
benzo[g,h,i]perylene	<b>1,23</b>	<b>1,10</b>	<b>1,03</b>	<b>1,03</b>	<b>1,01</b>	<b>1,03</b>	<b>1,03</b>	<b>1,03</b>
benzo[k]fluorantene	<b>1,24</b>	<b>1,14</b>	<b>1,17</b>	<b>1,17</b>	<b>1,16</b>	<b>1,17</b>	<b>1,17</b>	<b>1,17</b>
chrysene	<b>1,25</b>	<b>1,19</b>	<b>1,01</b>	<b>1,01</b>	1,00	<b>1,01</b>	<b>1,01</b>	<b>1,04</b>
dibenzo[a,h]anthracene	<b>1,29</b>	<b>1,24</b>	<b>1,12</b>	<b>1,13</b>	<b>1,12</b>	<b>1,11</b>	<b>1,12</b>	<b>1,17</b>
fluoranthene	<b>1,27</b>	<b>1,25</b>	<b>1,19</b>	<b>1,20</b>	<b>1,19</b>	<b>1,19</b>	<b>1,19</b>	<b>1,24</b>
fluorene	<b>1,17</b>	<b>1,09</b>	0,96	0,96	0,94	0,96	0,97	0,93
indeno[1,2,3-cd]pyrene	<b>1,22</b>	<b>1,08</b>	<b>1,11</b>	<b>1,12</b>	<b>1,10</b>	<b>1,11</b>	<b>1,11</b>	<b>1,14</b>
nafththalene	0,26	0,28	0,08	0,06	0,02	0,11	0,11	0,14
phenanthrene	<b>1,05</b>	<b>1,03</b>	0,83	0,82	0,82	0,85	0,84	0,79
pyrene	<b>1,26</b>	<b>1,18</b>	<b>1,11</b>	<b>1,12</b>	<b>1,11</b>	<b>1,11</b>	<b>1,12</b>	<b>1,13</b>
PCB28	0,93	0,93	<b>1,30</b>	<b>1,29</b>	<b>1,32</b>	<b>1,31</b>	<b>1,30</b>	<b>1,24</b>
PCB31	0,88	0,88	<b>1,27</b>	<b>1,25</b>	<b>1,27</b>	<b>1,27</b>	<b>1,27</b>	<b>1,17</b>
PCB52	0,88	0,82	<b>1,34</b>	<b>1,32</b>	<b>1,33</b>	<b>1,34</b>	<b>1,33</b>	<b>1,22</b>
PCB101	0,84	0,77	<b>1,30</b>	<b>1,29</b>	<b>1,29</b>	<b>1,30</b>	<b>1,30</b>	<b>1,18</b>
PCB118	0,84	0,78	<b>1,33</b>	<b>1,31</b>	<b>1,32</b>	<b>1,33</b>	<b>1,33</b>	<b>1,20</b>
PCB138	0,76	0,75	<b>1,29</b>	<b>1,27</b>	<b>1,31</b>	<b>1,29</b>	<b>1,28</b>	<b>1,28</b>
PCB153	0,82	0,75	<b>1,30</b>	<b>1,28</b>	<b>1,29</b>	<b>1,30</b>	<b>1,30</b>	<b>1,18</b>
PCB180	0,79	0,72	<b>1,26</b>	<b>1,25</b>	<b>1,26</b>	<b>1,26</b>	<b>1,26</b>	<b>1,17</b>

	C1-Naphalene	C2-Naphtalene
<b>Experimental variables</b>		
Coal (g) added	0,49	0,12
Water (mL) added	0,28	0,15
<b>Soil characteristics</b>		
% < 63 um	0,10	0,01
TOC (mg/g ts)	0,66	0,49
S1 (mg/g)	<b>1,01</b>	<b>1,02</b>
S2 (mg/g)	0,87	0,60
S3 (mg/g)	<b>1,30</b>	<b>1,40</b>
Tmax (°C)	0,75	0,69
HI	0,94	0,63
OI	0,41	0,66
HCB	<b>1,44</b>	<b>1,22</b>
acenaphtene	<b>1,05</b>	0,88
acenaphthylene	0,70	0,53
anthracene	<b>1,33</b>	<b>1,30</b>
benzo[a]anthracene	<b>1,08</b>	0,99
benzo[a]pyrene	<b>1,16</b>	<b>1,11</b>
benzo[b]fluorantene	<b>1,14</b>	<b>1,09</b>
benzo[g,h,i]perylene	<b>1,12</b>	<b>1,01</b>
benzo[k]fluorantene	<b>1,22</b>	<b>1,18</b>
chrysene	<b>1,11</b>	0,96
dibenzo[a,h]anthracene	<b>1,20</b>	<b>1,11</b>
fluoranthene	<b>1,19</b>	<b>1,15</b>
fluorene	<b>1,10</b>	0,91
indeno[1,2,3-cd]pyrene	<b>1,14</b>	<b>1,10</b>
nafhthalene	0,34	0,08
phenanthrene	0,93	0,72
pyrene	<b>1,19</b>	<b>1,09</b>
PCB28	<b>1,19</b>	<b>1,47</b>
PCB31	<b>1,14</b>	<b>1,41</b>
PCB52	<b>1,05</b>	<b>1,29</b>
PCB101	<b>1,01</b>	<b>1,24</b>
PCB118	<b>1,04</b>	<b>1,28</b>
PCB138	0,72	<b>1,04</b>
PCB153	0,98	<b>1,22</b>
PCB180	0,86	<b>1,11</b>

	Acen- aftylen	Acen- aften	Fluoren	Fen- antren	Antra- cen	Fluor- anten	Pyren	Benzo(a) antracen	Chrysen	Benzo(b,j) fluoranten	Benzo(k) fluoranten	Benzo(e) pyren	Benzo(a) pyren	Perylen	Indeno(1,2,3- cd)pyren	Dibenz (ac/ah)antracen	Benzo (ghi)perylene
Coal (g) added	0,51	0,32	0,76	0,71	0,76	0,53	0,45	0,37	0,21	0,25	0,05	0,45	0,03	0,08	0,05	0,06	0,16
Water (mL) added	0,35	0,33	0,34	0,29	0,19	0,17	0,17	0,40	0,36	0,48	0,42	0,67	0,27	0,25	0,35	0,57	0,27
% < 63 um	0,58	0,08	0,08	0,40	0,38	0,29	0,18	0,16	0,05	0,07	0,17	0,33	0,21	0,22	0,24	0,22	0,36
TOC (mg/g ts)	0,63	0,73	0,70	0,59	0,64	0,38	0,53	0,66	0,78	0,73	0,67	0,60	0,92	0,94	0,93	0,88	<b>1,04</b>
S1 (mg/g)	0,78	0,76	0,74	0,78	0,83	0,68	0,81	0,66	0,70	0,66	0,67	0,72	0,71	0,80	0,70	0,67	0,73
S2 (mg/g)	0,54	0,60	0,60	0,53	0,55	0,28	0,54	0,51	0,75	0,59	0,52	0,54	0,72	0,88	0,72	0,70	0,86
S3 (mg/g)	<b>1,24</b>	<b>1,33</b>	<b>1,39</b>	<b>1,56</b>	<b>1,36</b>	<b>1,58</b>	<b>1,44</b>	<b>1,47</b>	<b>1,31</b>	<b>1,41</b>	<b>1,43</b>	<b>1,31</b>	<b>1,25</b>	<b>1,18</b>	<b>1,22</b>	<b>1,16</b>	<b>1,15</b>
Tmax (°C)	<b>1,58</b>	<b>1,33</b>	<b>1,35</b>	<b>1,23</b>	<b>1,33</b>	<b>1,36</b>	<b>1,16</b>	<b>1,46</b>	<b>1,19</b>	<b>1,43</b>	<b>1,58</b>	<b>1,32</b>	<b>1,28</b>	<b>1,17</b>	<b>1,39</b>	<b>1,50</b>	<b>1,21</b>
HI	0,91	0,11	0,07	0,24	0,17	0,08	0,31	0,43	0,27	0,30	0,64	0,16	0,23	0,28	0,32	0,35	0,11
OI	0,78	0,45	0,63	<b>1,22</b>	0,82	0,93	0,66	0,76	0,30	0,58	0,73	0,81	0,12	0,03	0,10	0,13	0,13
HCB	0,71	0,86	0,89	0,91	0,97	0,85	<b>1,10</b>	0,76	<b>1,09</b>	0,81	0,72	0,98	0,82	<b>1,05</b>	0,79	0,78	0,85
acenaphthene	<b>1,12</b>	<b>1,24</b>	<b>1,21</b>	<b>1,02</b>	<b>1,16</b>	<b>1,07</b>	<b>1,11</b>	<b>1,15</b>	<b>1,24</b>	<b>1,20</b>	<b>1,17</b>	<b>1,16</b>	<b>1,26</b>	<b>1,30</b>	<b>1,30</b>	<b>1,31</b>	<b>1,31</b>
acenaphthylene	<b>1,46</b>	<b>1,32</b>	<b>1,34</b>	<b>1,08</b>	<b>1,25</b>	<b>1,21</b>	<b>1,06</b>	<b>1,38</b>	<b>1,19</b>	<b>1,40</b>	<b>1,52</b>	<b>1,30</b>	<b>1,30</b>	<b>1,24</b>	<b>1,45</b>	<b>1,62</b>	<b>1,30</b>
anthracene	<b>1,13</b>	<b>1,25</b>	<b>1,24</b>	<b>1,24</b>	<b>1,26</b>	<b>1,31</b>	<b>1,34</b>	<b>1,24</b>	<b>1,31</b>	<b>1,24</b>	<b>1,19</b>	<b>1,22</b>	<b>1,25</b>	<b>1,27</b>	<b>1,21</b>	<b>1,14</b>	<b>1,22</b>
benzo[a]anthracene	<b>1,24</b>	<b>1,30</b>	<b>1,26</b>	<b>1,13</b>	<b>1,23</b>	<b>1,19</b>	<b>1,18</b>	<b>1,22</b>	<b>1,24</b>	<b>1,24</b>	<b>1,25</b>	<b>1,18</b>	<b>1,29</b>	<b>1,29</b>	<b>1,32</b>	<b>1,30</b>	<b>1,31</b>
benzo[a]pyrene	<b>1,18</b>	<b>1,23</b>	<b>1,20</b>	<b>1,14</b>	<b>1,23</b>	<b>1,24</b>	<b>1,26</b>	<b>1,23</b>	<b>1,28</b>	<b>1,24</b>	<b>1,21</b>	<b>1,21</b>	<b>1,26</b>	<b>1,25</b>	<b>1,23</b>	<b>1,18</b>	<b>1,24</b>
benzo[b]fluorantene	<b>1,16</b>	<b>1,22</b>	<b>1,19</b>	<b>1,11</b>	<b>1,19</b>	<b>1,21</b>	<b>1,23</b>	<b>1,23</b>	<b>1,28</b>	<b>1,25</b>	<b>1,22</b>	<b>1,16</b>	<b>1,28</b>	<b>1,27</b>	<b>1,26</b>	<b>1,20</b>	<b>1,27</b>
benzo[g,h,i]perylene	<b>1,11</b>	<b>1,19</b>	<b>1,16</b>	<b>1,04</b>	<b>1,16</b>	<b>1,10</b>	<b>1,16</b>	<b>1,14</b>	<b>1,24</b>	<b>1,18</b>	<b>1,14</b>	<b>1,11</b>	<b>1,24</b>	<b>1,28</b>	<b>1,24</b>	<b>1,20</b>	<b>1,27</b>
benzo[k]fluorantene	<b>1,15</b>	<b>1,24</b>	<b>1,22</b>	<b>1,17</b>	<b>1,23</b>	<b>1,28</b>	<b>1,29</b>	<b>1,25</b>	<b>1,31</b>	<b>1,26</b>	<b>1,22</b>	<b>1,23</b>	<b>1,26</b>	<b>1,26</b>	<b>1,23</b>	<b>1,17</b>	<b>1,24</b>
chrysene	<b>1,13</b>	<b>1,24</b>	<b>1,21</b>	<b>1,06</b>	<b>1,19</b>	<b>1,14</b>	<b>1,17</b>	<b>1,20</b>	<b>1,28</b>	<b>1,24</b>	<b>1,21</b>	<b>1,14</b>	<b>1,29</b>	<b>1,33</b>	<b>1,32</b>	<b>1,31</b>	<b>1,32</b>
dibenzo[a,h]anthracene	<b>1,22</b>	<b>1,30</b>	<b>1,29</b>	<b>1,20</b>	<b>1,29</b>	<b>1,30</b>	<b>1,29</b>	<b>1,29</b>	<b>1,33</b>	<b>1,31</b>	<b>1,29</b>	<b>1,25</b>	<b>1,30</b>	<b>1,32</b>	<b>1,31</b>	<b>1,29</b>	<b>1,30</b>
fluoranthene	<b>1,22</b>	<b>1,30</b>	<b>1,28</b>	<b>1,21</b>	<b>1,27</b>	<b>1,30</b>	<b>1,28</b>	<b>1,28</b>	<b>1,30</b>	<b>1,29</b>	<b>1,27</b>	<b>1,23</b>	<b>1,30</b>	<b>1,29</b>	<b>1,29</b>	<b>1,25</b>	<b>1,29</b>
fluorene	0,97	<b>1,14</b>	<b>1,11</b>	0,95	<b>1,05</b>	0,91	<b>1,00</b>	0,99	<b>1,13</b>	<b>1,05</b>	<b>1,01</b>	0,97	<b>1,17</b>	<b>1,26</b>	<b>1,21</b>	<b>1,18</b>	<b>1,26</b>
indeno[1,2,3-cd]pyrene	<b>1,21</b>	<b>1,21</b>	<b>1,19</b>	<b>1,15</b>	<b>1,24</b>	<b>1,26</b>	<b>1,27</b>	<b>1,23</b>	<b>1,27</b>	<b>1,24</b>	<b>1,21</b>	<b>1,22</b>	<b>1,23</b>	<b>1,23</b>	<b>1,21</b>	<b>1,16</b>	<b>1,20</b>
naftthalene	0,66	0,21	0,24	0,58	0,33	0,36	0,07	0,39	0,20	0,22	0,45	0,38	0,31	0,44	0,33	0,33	0,48
phenanthrene	0,82	<b>1,01</b>	0,97	0,79	0,87	0,68	0,80	0,85	0,99	0,92	0,87	0,83	<b>1,08</b>	<b>1,15</b>	<b>1,12</b>	<b>1,10</b>	<b>1,20</b>
pyrene	<b>1,14</b>	<b>1,25</b>	<b>1,23</b>	<b>1,12</b>	<b>1,21</b>	<b>1,18</b>	<b>1,21</b>	<b>1,19</b>	<b>1,27</b>	<b>1,22</b>	<b>1,18</b>	<b>1,16</b>	<b>1,27</b>	<b>1,30</b>	<b>1,27</b>	<b>1,23</b>	<b>1,29</b>
PCB28	0,89	0,96	0,94	<b>1,08</b>	0,93	<b>1,19</b>	<b>1,17</b>	<b>1,06</b>	<b>1,03</b>	<b>1,01</b>	0,95	0,91	<b>1,04</b>	0,90	0,90	0,81	0,95
PCB31	0,85	0,90	0,88	0,99	0,88	<b>1,10</b>	<b>1,10</b>	0,99	0,99	0,96	0,89	0,89	0,99	0,86	0,85	0,79	0,91
PCB52	0,83	0,88	0,86	0,96	0,85	0,95	0,97	0,84	0,84	0,82	0,79	0,97	0,82	0,75	0,75	0,73	0,76
PCB101	0,78	0,83	0,81	0,93	0,81	0,88	0,92	0,77	0,77	0,76	0,74	0,96	0,74	0,68	0,68	0,69	0,68
PCB118	0,78	0,84	0,82	0,95	0,81	0,92	0,94	0,79	0,79	0,77	0,74	0,97	0,74	0,68	0,68	0,68	0,68
PCB138	0,82	0,80	0,76	0,92	0,74	0,89	0,80	0,76	0,64	0,71	0,72	0,90	0,69	0,57	0,63	0,61	0,61
PCB153	0,76	0,82	0,80	0,92	0,78	0,86	0,89	0,75	0,74	0,73	0,71	0,95	0,70	0,65	0,65	0,66	0,65
PCB180	0,76	0,79	0,76	0,89	0,75	0,81	0,82	0,72	0,67	0,70	0,69	0,92	0,67	0,61	0,63	0,64	0,62