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# FORENSIC GEOCHEMISTRY AS TOOL TO SUPPORT ENVIRONMENTAL LIABILITY INVESTIGATIONS – A CASE STUDY FROM A FUEL STATION IN GERMANY

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**Abstract.** *For a definite declaration of the pollution causer results of a conventional investigation is in many cases insufficient. The detected pollutants are often on the first view identical and therefore cannot assign conclusively to one of the potential causers. This is particularly the case if there are several users at the same location, but at different times operating. For such problems the analytics offers proceeding methods to examine the origin and age of contaminations. The present case study has the investigation of soil pollution in Berlin-Neukölln, Germany in the focus to assess the pollution cause. The studied object is a former fuel station with BTEX and TPHs pollution. For the characterization and the dating of the pollutions were investigated the hydrocarbon composition in soil and water as well as the biomarker distribution patterns and lead isotope compositions.*

**Keywords:** causer of soil pollution, environmental liability, fuel pollution

## Introduction

In April 2004, the Directive 2004/35/EC on environmental liability with regard to the prevention and remedying of ecological damage came into force (Directive, 2004). According to § 3 the scope of the Environmental Liability Directive is limited to the security for soil and water as well as protected species and natural habitats. Germany implemented the requirements of the Environmental Liability Directive with the Environmental Liability Law (last update 23 Nov. 2007, I, p. 2631, 2670). The Directive constitutes a public responsibility of the contributors to ecological damage, and the corresponding powers of intervention of the authorities. In this way it brings innovations to the German law at some points, in particular in terms of strengthening of the polluter pays principle.

For a clear identification of the causer the damage, the results of historical and conventional technical exploration in many cases are not enough. The pollutants

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found are identical at first glance, and can thus be assigned to any of the potential interferers conclusive. This is especially true when several causers acted in the same location, but were consecutively active. The analysis of such problems provides further methods for investigation on the origin and age of contaminants. Searching for a special group of substances or isotope distributions, comparable to a detective search for traces of fingerprints, is the scope of forensic geochemistry.

Philp (2007) defined “Environmental Forensics” as a scientific methodology developed for identifying petroleum-related and other potentially hazardous environmental contaminants and for determining their sources and time of release. It combines experimental analytical procedures with scientific principles derived from the disciplines of organic geochemistry and hydrogeology. Forensic geochemistry begins where common environmental procedures do not deliver detailed results, due to their limitation in description and quantification (Philp, 2007).

In case of success, with forensic geochemistry primary conditions are met to identify the source, the time and the causer of contaminations, by attempting to answer questions with specific chemical programs and methods: What? Where? Wherefrom? When? Who? Comparable to a criminalistic search for fingerprints, on this occasion special element groups or isotope distribution are investigated (Lewis et al., 2004; Peters and Moldowan, 1993). From the occurrence of characteristic patterns, conclusions about the history of the pollutants, i.e. their input and behaviour in the subsoil, can be drawn (Kaplan et al., 1997). The main scope of forensic geochemistry methods is to find out the cause and the causer of an environmental pollution to solve cases of environmental liability. Main users are environmental liability insurances.

## Methodological Approach

### *Scope and Location*

The study area is a former gas station in Berlin-Neukölln, which was in operation since the 1950s. The area is geologically located in the outermost region of a glacial valley. There were several rebuilding and changes on the location by the operator. In November 2007 the location was closed and, in preparation for dismantling, the side was comprehensively investigated (samples from 25 drilling cores, as well as analytical investigations on total petroleum hydrocarbon (TPH), benzene, toluene, ethylbenzene, and xylenes (BTEX), and methyl tertiary butyl ether (MTBE)). An overview of the local situation is given in Fig. 1.

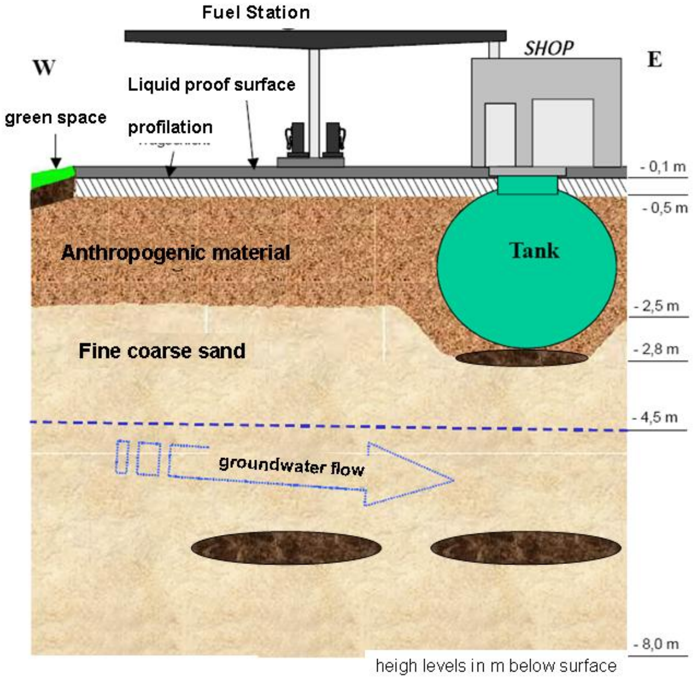

**Fig. 1.** Schematic situation of the local situation at the former fuel station

A contamination with TPH concentrations ranging from 1.000 to 10.000 mg/kg was detected in two areas at about 6 m below ground level. These two types of pollutant sources are the area of the former separators as well as the area of the former petrol depot. The groundwater level was detected at 4.5 m below ground. Due to the risk that the TPHs (and partially BTEX) could also be mobilized in the polluted parts, the risk minimization strategy after evaluation of the dimension of the pollutant source considered the removal of polluted soil material (Fig. 2). The scope of the further investigation at the site was to verify who is responsible for the contamination and finally to whom to allocate the cost for the remediation.

**Fig. 2.** Soil removal from the area of the former petrol depot at the former fuel station

## Methodological Basics

The production process of many current pollutants (for example TPHs) changed in the course of time. This results in regional and chronological cycles, which are indicated by typical patterns (Philp, 2007; Kaplan and Galperin Y., (1996), Kaplan et al., 1996; Kaplan et al., 1997; Stout, 1998). The isotopic composition of the raw materials used in the past helps nowadays to identify these patterns (Philp, 2007). In case of contaminations it is possible, for example by the quantification of stable hydrogen- and carbon isotopes (isotope-fingerprint), to investigate the method of production of the organic pollutant and therefore the time period it was produced and released in the environment (Philp, 2007). It is also of interest, if a pollutant was released in the environment by natural or technical processes. This can be estimated by isotope investigations of heavy metals or mineral salts. For example, lead from gasoline (diffuse input) has a different isotope-fingerprint compared to geogenic lead (Durali-Müller, (2005); Kim et al., 2013).

Gasoline is often released in the subsoil on gas stations by overfilling or leak gasoline pipes. Conclusions about the age of such contaminations can be drawn by the identification of typical fuel-additives (lead compounds, halogenic organic substances, MTBE) in soil or groundwater samples (Effenberger et al., 2001; Schirmer et al., 2003). Thus the occurrence of the pollution can be limited to a certain time period. For such investigations at TPHs pollutions primary soil samples are adequate. For the detection of the lead isotopic composition water as well as soil samples are practicable. The differentiation is only possible for West-German gasoline.

The dating of TPHs pollution is limited to the anaerobe degradation and is retraceable for a maximum of 25 years. For this approach, data of the geochemical environment should be provided. As dating criteria for diesel/heating oil the C17/Pristan-relation is used. The lead isotopic composition allows a classification of the gasoline contamination before 1975 and after 1978 in the area of West-Germany. By the determination of the respiration activity in soil material conclusions can be drawn about the microbial activity in the soil. The determination of single hydrocarbons is used for the characterization of the contamination on the one hand and, on the other hand, for the dating. For the dating the relations of certain organic substances, which are characteristic for the process of degradation, were determined. This includes the ratios of:

***Pristane/ Phytane***

The compounds are degradation products of long-chain hydrocarbons. The portion of phytane (n-C18-) compared to pristane (n-C17-) increases with an increasing age of the pollution (practicable for diesel/heating pollution).

***BTEX (benzene, toluene/ethylbenzene, xylenes)***

Benzene/toulene degrades much faster than ethylbenzene/xylene. Because of their short chain length they are also more volatile due to leaching and evaporation.

***Iso- and n-alkenes***

In hydrocarbons iso- and n-alkenes are present in similar ratios. The microbial decomposition of the n-alkenes is clearly faster compared to the iso-alkenes. Using the ratio between both groups a conclusion about the degradation process can be drawn.

***MTBE***

MTBE (Methyl tert-butyl ether) was added to gasoline as an antiknock additive, to guarantee a minimum content of oxygen and as a substitute for aromatic substances in unleaded gas. Thus the emissions into the environment should be reduced.

***Pb-isotopic composition***

The lead in the soil is a mixture of different lead isotopes. The stable isotopes are of radiogenic origin, except the isotope $^{204}$Pb, the isotopes $^{206}$Pb, $^{207}$Pb and $^{208}$Pb. This means they are evolved from the radioactive decay series of the elements uranium and thorium. Because of the different geological ages and the different amount on uranium and thorium, which depends on the deposit, lead from different ore deposits shows a clearly different specific lead isotope ratio [9]. This characteristic isotope signature is also preserved during afterwards occurring natural transformations (rock weathering and transport processes) [13]. Thus, the lead from soil minerals of a certain region shows a specific geogenic isotope ratio. In contrast the lead in industrial materials (for example munitions, dye, varnish, gas-lead, lead crystal etc.) is characterized by isotope ratios, which are clearly different from regional geogenic ones.

The dating of pollution with TPHs depends on the location and has to include several environmental parameters like, for example the composition of the basic product, the hydrogeological conditions, temperature and water content of the unsaturated soil as well as the permeability, the redox potential and the nutrient availability. Figure 3 Table 1 shows schematically the characteristic alterations of a mineral oil product during the degradation in the subsoil.

**Table 1.** Steps of the microbial degradation of TPHs (modified after Peters and Moldowan, 1993; Kaplan et al., 1997)

| **Level of biodegradation** | **Chemical composition** | Increased Biodegradation ↓ |
|---|---|---|
| 1 | n-alkane unchanged | |
| 2 | highly volatile alkanes were removed | |
| 3 | alkane in the middle range, olefines, benzenes and toluenes were removed | |
| 4 | more than 90% of the n-alkanes were removed | |
| 5 | alkylcyclohexanes and alkylbenzenes were removed;<br>isoprenoids and naphthalene were partially removed | |
| 6 | isoprenoids, $C_1$-naphthalene, benzothiophenes and alkylbenzothiophene were removed;<br>$C_2$-naphthalene selectively partially removed | |
| 7 | dibenzothiophenes, phenanthrenes and other PAH selectively partially removed | |
| 8 | tricyclic terpanes enriched; selected regular steranes were removed; $C_{31}$-$C_{35}$ homohopane partially removed | |

| | | |
|---|---|---|
| 9 | tricyclic terpanes, diasteranes and aromatic steranes are enriched | |

The TPHs in the soil underlie mostly secondary alterations, which comprise four processes: evaporation, biological degradation, leaching and polymerization. The nature and extent of the alterations depends on the external conditions (climate, soil, soil/groundwater conditions) and the composition of the hydrocarbons. In this context the biological degradation strongly depends on the oxygen supply and the microbial activity in the soil. According to the conditions, the degradation processes can occur fast or for decades. Microorganisms with the ability to degrade TPHs are ubiquity and grow rapidly in the soil under suitable conditions. In most cases the microbial degradation involves the leaching of TPHs. The leaching of TPHs is related to the water solubility of the molecules. Aromates are more mobile compared to polycyclic alkanes.

For the categorization of the degradation level after Table 1, it is necessary to work out in what amount the readily degradable substances are still present and in what extent the poorly degradable substances are already enriched. Because of a potential overlapping caused by a possible mixed contamination, the age of the younger component can only be estimated by the distribution pattern and enrichment level of the easily degradable substances. Contrary, only the distribution pattern and the enrichment level of the poorly degradable substances are suited to determine the residence time of the older components. The following indications are relatively attributed to younger components or suitable for their dating:

- n-alkanes in the range C13-C23 are detectable despite low concentrations, n-alkanes below C13 are already absent
- isoprenoides above i-C15 are still present, whereas thus below i-C15 are already absent
- strong dominance of pristane and phytane above n-C17 and n-C18, respectively
- low values of alkylbenzenes, naphtalenes and benzothiophenes.

Beside the development of the characteristic, unresolved slope in the latter part of the total ion current chromatogram (“lubricating oil slope”), also the following findings can be helpful to derive the age of older components:

- relative enrichment of diasteranes,
- relative enrichment of tricyclic terpanes,

- strong enrichment of monoaromatic steranes, pyren and chrysen as well as low values of 2 – 3 cycle PAH,
- low values of sulphurous thiophenes.

## Investigation Program

### *Scope and Location*

The studied object is a former fuel station areal in Berlin-Neukölln with a BTEX and TPHs pollution. There are two point source areas of the pollution, as described below. From both sites were taken samples, as well as an upstream reference sample.

- sampling point $\mathbf{A}_{PA}$ – pollution source in the north-eastern part of the side (gasoline **p**ump **a**rea)
- sampling point $\mathbf{B}_{FD}$ – pollution source in the south-western part of the side (former **f**uel **d**epot)
- sampling point $\mathbf{C}_{UP}$ – **up**stream reference sample.

According to the information of the preliminary surveys the pollution sources are diesel and gasoline pollutions. For the characterization and the dating of the pollutions the following types of investigations were performed:

- characterisation of the type of hydrocarbons,
- fingerprint of the biomarker distribution pattern,
- lead examinations for the dating of gasoline.

Following analysis were carried out:

- dry residue, water retention capacity and respiration activity
- content of BTEX, TPHs and lead,
- pristan/phytan ratio with GC-MS,
- organic overall analysis with GC-MS,
- lead isotopic composition of gasoline.

**Fig. 3.** Soil and soil gas sampling at the former fuel station.

The investigations of the lead in the samples, with regard to the lead isotopes, allow for drawing further conclusions of the source and the age of the pollution. To derive the origin of the lead concentration samples of contaminated soil a reference soil sample was determined in terms of the lead isotope ratios and, with respect to a possible geogenic or anthropogenic source, and compared with data from literature. Moreover potential mixture relations were evaluated. Additional investigations on the stable carbon isotope $^{13}C$ of the soil gas were performed.

***Investigation Program***

The following investigations on the samples were performed to characterize the contamination:

***Determination of the total content:***

- mineral oil hydrocarbons TPHs with GC-method (H 53),
- aromatic hydrocarbons (BTEX) with GC-MS,
- lead scavenger (EDB and EDC) with GC –MS,
- methyl tert-butyl ether (MTBE) with GC-MS.

Thereafter for both, the soil sample and the oil samples of the study side, the contamination was characterized by GC/MS fingerprinting. For the soil sample the extraction was carried out with methylene-chloride and a following separation of the polar substances from the extract by column chromatography.

***Characterization of the contamination by biomarker distribution patterns:***

Detailed GC-MS analytics of

- total ion current chromatogram (TIC),
- n-alkanes (m/z 85 chromatogram),
- alkylcyclohexanes (m/z 83 chromatogram),
- iso-alkanes and isoprenoides (m/z 113 chromatogram),
- C4-alkylbenzole (m/z 134 chromatogram).

Thereafter for both the soil and water samples of the study side the contamination was characterized by GC/MS fingerprinting. For the soil sample the extraction was carried out with methylene-chloride and a following separation of the polar substances from the extract by column chromatography.

In the frame of the sampling moreover the following samples were taken:

| | |
|---|---|
| $C_{UP}$ | Pb isotopic composition |
| $B_{FD}$ | Pb isotopic composition |
| $A_{PA}$ | reserve sample for Pb isotopic composition |
| $B_{FD}$ | upper part: soil gas (C1-C1, $CO_2$, $O_2$, $^{13}C$-$CH_4$, $^{13}C$-$CO_2$) |
| $B_{FD}$ | lower part: soil gas (C1-C1, $CO_2$, $O_2$, $^{13}C$-$CH_4$, $^{13}C$-$CO_2$). |

Additionally at the bottom of the excavation pit a water sample was taken.

### *Analytic and Assessment Procedure*

The determination of the TPHs contents included the chain length from C10 – C40. For this, both the detection by flame ionisation detector (FID) and by mass spectrometry (MS) is possible, whereas the mass spectrometry is more sensitive und more selective. The lighter hydrocarbons can be detected by the headspace-GC, which is also used to determine BTEX. For the investigation of the present samples all of the three analytic methods were applied. For the detection of the volatile components the headspace technique and the FID-evaluation were used. The more stable hydrocarbons were detected by GC-FID and GC-MS.

The sequence of the peaks in the chromatogram correlated with the chain length and the size of the molecules of the compound. The evaluation is made by standard chromatograms and calibrations. For this, defined concentrations of the examined substance were measured under the same conditions. To characterize the type of the TPHs contamination, first of all it was determined, which type of fuel causes the contamination. Gas includes hydrocarbon with a chain length from C5 – C12, Diesel includes hydrocarbon with a chain length from C9 – C24 and lubricating oil the range > C20. All three groups contain beside the n- and iso-alkanes about 5 – 10 % aromates of the particular chain length. Diesel and heating oil additionally contain high amounts of sulphurous components.

The determination of the $\delta^{13}C$ values of methane and carbon dioxide was done by Purge-and-Trap and GC Combustion Isotope Ratio Mass Spectroscopy (P&T-GC-C-IRMS). The concentrations of the compounds methane, ethane, propane, and i- as well as n- butane were detected by gas chromatography with flame ionisation detection. Oxygen was detected by gas chromatography with the thermal conductivity detection.

## Results

### *Analytical Results*

### *Determination of total contents*

Table 2 shows the results of the analytics of the total content investigations of organic substances.

**Table 2.** Composition of the results of the analytics of the total content investigations of organic substances

| ***Parameter*** | ***unit*** | ***Area of the former separators*** | | ***Area of the former petrol depot*** | | |
|---|---|---|---|---|---|---|
| | | $B_{FD}$ soil | $B_{FD}$ soil | $A_{PA}$ soil | unit | $A_{PA}$ water |
| Dry residue | % | 83.0 | 88.7 | 83.9 | | |
| Respiration acitivity | $mgO_2/g$ | <0.1 | <0.1 | <0.1 | | |
| BTEX | mg/kg | <0.01 | 15.92 | <0.01 | µg/l | <0.1 |
| Benzene | mg/kg | <0.01 | <0.01 | <0.01 | µg/l | <0.1 |
| Toluene | mg/kg | <0.01 | 0.079 | <0.01 | µg/l | <0.1 |
| Ethylbenzene | mg/kg | <0.01 | 0.62 | <0.01 | µg/l | <0.1 |
| m/p-Xylene | mg/kg | <0.02 | 10.03 | <0.02 | µg/l | <0.1 |
| o-Xylene | mg/kg | <0.01 | 5.19 | <0.01 | µg/l | <0.1 |
| TPHs | mg/kg | 12 | 11 | 16 | µg/l | 12 |
| MTBE | mg/kg | <0.01 | <0.01 | <0.01 | µg/l | 3.000 |

In the examined soil samples the TPHs contents ranged from 11 – 16 mg/kg. Beside the low TPHs content, the soil samples $A_{PA}$ and $B_{FD}$ show no findings of aromatic hydrocarbon (BTEX/MTBE). To determine these low levels in a high quality 100 g of sample material were used for extraction. For the sample $A_{PA}$ this can be explained by the largely removal of the contaminated soil and was expected. Here, the water sample, which clearly shows a phase, was taken on-site for detection. The samples had a characteristic smell of hydrocarbon, but only very low contents of TPHs of 11 and 12 mg/kg. This is not extraordinary, since TPHs show an intensive odour formation even in small traces. Relevant MTBE concentrations of 3.000µg/L were detected in the organic phase of the water sample. In the soil samples were no indications of existing lubricating oil. The characteristic “lubricating oil slope” in the GC-MS-chromatogram between 20-24 min. retention time was only detectable in the water sample $A_{PA}$ (indication of an older contamination). Also here compounds >C25 were missing. The GC-FID- and the headspace chromatogram show clearly, that only hydrocarbon in the range from <C10 to max. C15 are detectable in the samples. In the samples BTEX-aromates were measured, which clearly shows, that the contamination consists of light distillates. The MTBE amount found in the water sample indicates unleaded gasoline. The lacks of the middle hydrocarbon fraction as well as sulphurous substances support the assumption that this is not a diesel contamination. Thus the contamination can be explicitly characterized as a hydrocarbon contamination by gasoline.

### *Respiration activity*

The respiration activity indicates the oxygen demand in a sample for the biological transformation of the containing organic substance under optimized conditions (oxygen amount, temperature). It is described for a certain time period, for example four days as AT4. The resulting oxygen demand of the material, determined by the respiration activity, can be used as an indicator for the existing emission potential. The determination of the respiration activity showed a microbial activity below the detection limit. This is indicative either for a very slow microbial decomposition of the hydrocarbons at this side or for a low microbial activity.

### *Soil Gas Composition*

To derive the soil milieu, for the soil gas samples the gas composition and the $^{13}C$ values of $CH_4$ and $CO_2$ were determined. Table 3 shows the results of the measurements of the soil gas composition.

**Table 3.** Results of the investigations of the gas composition

| *Name* | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $i$-$C_4H_{10}$ | $n$-$C_4H_{10}$ | $O_2$ | $CO_2$ | $\delta^{13}C$-$CH_4$ | $\delta^{13}C$-$CO_2$ |
|---|---|---|---|---|---|---|---|---|---|
| | vpm | vpm | vpm | vpm | vpm | % | % | ‰-VPDB | ‰-VPDB |
| Upper | 8.5 | 1.2 | 1.6 | 2.9 | 16.3 | 20.2 | 0.45 | n.d. | - |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| sample $B_{FD}$ | | | | | | | | | 22.6±0.7 |
| Lower sample $B_{FD}$ | 6.1 | <0.1 | 0.1 | 0.4 | 2.2 | 20.4 | 0.16 | n.d. | - <br>20.8±0.7 |

n.d. = not detectable

### *Lead Isotope Ratios*

Table 4 shows the results of the measurements of the lead isotope ratios, Fig. 4 the comparison with literature data on the origin of lead isotope data.

**Table 4.** Results of the examination of the lead isotope ratio of the groundwater and of measurements from the upstream area.

| *Name* | $^{208}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{206}Pb/^{204}Pb$ | $^{208}Pb/^{207}Pb$ | $^{206}Pb/^{207}Pb$ |
|---|---|---|---|---|---|
| $C_{UP}$ | 39.6 ± 01 | 15.87 ± 0.04 | 20.37 ± 0.05 | 2.491 ± 0.001 | 1.2835 ± 0.00071 |
| $B_{FD}$ | 39.1± 0.1 | 15.75± 0.04 | 20.03 ± 0.04 | 2.485± 0.001 | 1.2724± 0.0006 |

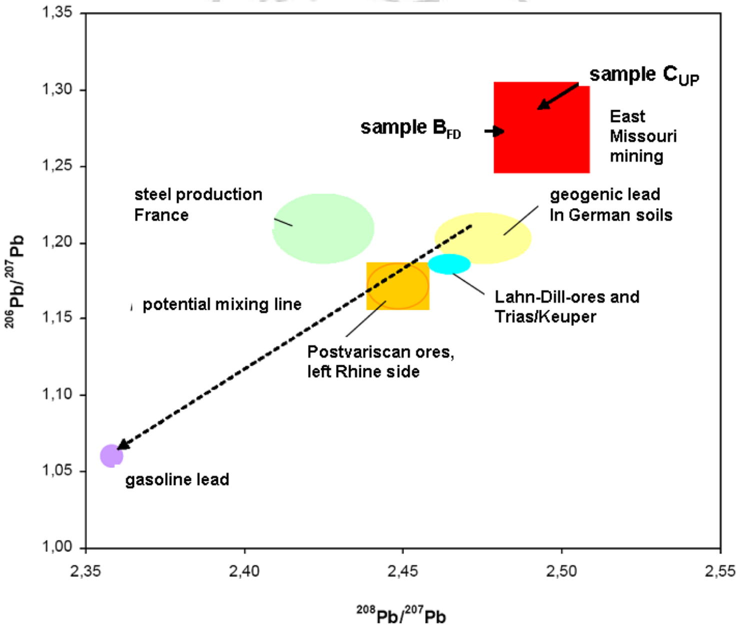

**Fig. 4.** $^{206}Pb/^{207}Pb$ ratio as a function of the $^{208}Pb/^{207}Pb$ ratio of analyzed samples.

### *Assessment of the Soil Data*

The low mineral oil concentrations indicate, especially for the area of the former separator which was not excavated at the date of sampling, that a strong degradation process has already occurred. The chromatograms of the single GC-detection show, that n- and iso-alkanes were almost completely removed. Further, the alcylcyclohexenes and alcylbenzenes are not detectable. Isopreniodes and napthalenes were not yet degraded. Benzene was only present in traces, toluene was not detectable. By means of the analytic parameters of the organic components and considering the low respiration activity, for the present study it can be concluded, that the substantial part of the biological degradation is already completed. Moreover, the decomposition of the TPHs contamination was obviously also driven by leaching and evaporation (good permeability of the sediments).

Considering the schematic process of the microbial degradation of TPHs, it can be concluded that the contamination is of a middle age, since the alcylcyclohexenes and alcylbenzenes are not detectable and the n- and iso-alkanes are almost completely degraded. The following criteria support that the investigated contaminations consists of a comparatively aged TPH product:

- n-alkanes are nearly completely removed,
- isoprenoides are besides the n-alkanes over the whole spectrum (i-C10 to phytan) clearly visible,
- alcylcyclohexenes and C4-alcylbenzenes are also degraded.

According to Kaplan et al. (1997) this corresponds with degradation level 5. The chronological contamination limitation was calculated with the time approximation algorithm according to Kaplan (1996), according to Eq. (1).

$$Rb = (B+T) / (E+X) \qquad (1)$$

For the sample $B_{FD}$ a value of 0,005 was calculated. After Kaplan values between 1.5 and 6 indicate an instantaneous occurrence of the contamination, values lower than 0.5 indicate residence times of >10 years. Another method for the chronological contamination limitation is the determination of the pristane/phytane ratio in fuels and heating oils. Pristane and phytane were not detected in the examined samples, since it was a gasoline contamination caused by a leakage of hydrocarbons with a chain length up to C12. The degradation is carried out by leaching, biodegradation and evaporation, not by condensation. Thus, no long chained C17/C18 molecules were detectable.

In the water sample all BTEX-aromates were degraded completely and partly also removed by leaching and evaporation. There were no BTEX detectable, however a high content of MTBE. Since the 1980s MTBE has become increasingly important as mixing component in gasoline (octanbooster). The first large-scale facilities for the production were put into operation at the end of the 1970s in Italy and Germany. The existing of MTBE in the examined sample indicates that the TPHs contamination consists of substances, which have been used in Germany since 30 years. The high content of MTBE points to an originally high contamination. Because of the existence of MTBE and barely detectable BTEX, in the water $A_{PA}$ sample a microbiological degradation can be assumed. MTBE acts quite similar to BTEX-aromates referring to water solubility and volatility, however it is less degradable.

As in the soil samples all n- and iso-alkanes as well as the easy microbial degradable aromates are not detectable or exist only in traces. The still existing hydrocarbons in the sample are visible in the screenings. These are mainly aromatic compounds of a moderate chain length. The most of these are substituted with amino groups, indicating a biological degradation. After Kaplan et al. (1997) this state corresponds to the degradation level 6. Thus, a contamination with a residence time >10 a can be concluded. This is confirmed by a comparison with several studies on MTBE and BTEX contaminations in Germany (Effenberger et al., 2001; Schirmer et al., 2003; Martienssen et al., 2003; Martienssen et al., 2006). On contaminations at the age of 5 – 10 years, there was a proceeding degradation of BTEX along with high MTBE concentrations. Only for older contaminations there were reduced amounts of MTBE because of their slow degradability.

The examination of the lead in the soil regarding to the lead-isotopes can enable further conclusions about the date of the contamination. The lead concentrations can have different sources like recent seepage water of a waste disposal, industry waste (for example foundry sand, munitions) or lead from the dust of traffic and urban rainwater (for example gas lead), respectively. As the source of the lead in the examined samples lead residues were presumed, since the study side was a former fuel station. The predominantly alkyl lead compounds (adding of MTBE as antiknock additive) used in Germany between 1976 and about 1990 in Germany originate from Australia and show a signature with relative low radiogenic isotope ratios. Before 1972 European lead (for example from Yugoslavia) was used for the production of alkyl lead compounds.

The content of lead isotopes of both examined samples is not in the range of the common industrial lead in Western Germany. The lead isotope ratios are also not in the range of geogenic, hence rock and soil lead in Europe. Deposits with such high radioactive lead are found in East-Missouri (USA). It is noticeable, that this American lead isotope signature is even in the upstream sample clearly visible. Due to the lead isotope signature of the samples it must be concluded, that the portion of lead used in Germany is very low. Because of the very low lead concentration it can be concluded, that there is no significant portion of leaded gasoline. Thus, the measured concentrations in the soil are almost certainly to interpret as inputs for example from battery lead or munitions lead originating from America what is in accordance to the fact that Berlin-Neukölln was a very heavily bombarded area in the so called American sector in the World War II.

### *Origin and Determination of the Soil Gas*

Natural gases can derive from two primary processes. One of these processes is of biological nature (production by bacteria), the other one is of thermogenic nature (creation by thermal decomposition of organic material in the covered organic rich sediments). Potential explosive gasses, like $CH_4$ or toxic gasses like $H_2S$ can outgas from the soil.

***Methane of bacterial origin:*** Methanogenic bacterias participate with other bacterias on the degradation of organic material under strictly anaerobe conditions, like in lakes, estuaries, marine sediments and water saturated soils. During this process for example hydrogen sulphide, carbon dioxide, organic acids, ketones are formed by fermentation and enzymatic reactions. At places, where simple organic acids, like acetic acid are formed, methanogenic bacteria are able to form methane under significant anaerobe conditions by fermentation:

$$CH_3COOH \xrightarrow[\text{methanogenic bacteria}]{} CH_4 + CO_2 \tag{2}$$

Fermentative methane production happens usually in waste disposals and organic rich fresh water system, in which organic acids are produced.

Besides the fermentation reaction also the $CO_2$ reduction can entail the production of methane. Traces of ethylene can exist.

$$CO_2 + 4H_2 \xrightarrow[\text{methanogenic bacteria}]{} CH_4 + H_2O \tag{3}$$

***Thermogenic methane:*** When organic material, which is enriched in covered sediment layers and is under the influence of the geothermal gradient (~3°C/100 m), in a depth of 2.200 to 2.800 m a decomposition of the organic occurs. This begins with a thermal decomposition of methane, gaseous hydrocarbons, carbon dioxide and water with temperatures above 70°C. Formerly thermogenic gasses contain ethane and other volatile hydrocarbons but no ethane. At higher temperatures (>150°C) methane becomes the main component of the gas. If methane is the single hydrocarbon component in the gas, no conclusions about the origin of the gas can be drawn on the basis of the residual gas composition.

The concentration of the hydrocarbons in the samples is very low. The main component in the samples is oxygen. The $CO_2$ concentration exceeds clearly the air concentration. The gas is a typical soil gas with traces of hydrocarbons. The clear detection of butane indicates a degradation of MTBE. Methane, which is detected at a concentration of 6.1 and 8.5 vpm, can originate from the soil or from the splitting of from higher hydrocarbons (MTBE). This is also indicated by the low traces of ethane and propane. The measured $\delta^{13}C$- $CO_2$ value of 22.6 an 20.8 ‰, respectively are in the typical range of $\delta^{13}C$- $CO_2$ values for soil gas. Because of the low concentration of hydrocarbons it can not differentiated, whether the $CO_2$ is formed by acetate splitting or it is remained $CO_2$ of the $CO_2$ reduction or it origins from the soil organic.

## Conclusions

Investigations on the characterization and the dating of TPHs contaminations in Berlin-Neukölln were performed. Two polluted localities were differentiated:

- Contaminations in the northeast part of the location, the former gasoline pump area (represented by the soil samples $B_{FD}$) and
- Contaminations in the area of the former gasoline depot (represented by the soil sample $A_{PA}$ Soil and the water sample $A_{PA}$ Water).

Both locations were investigated regarding to their total contents and the characteristics of the contaminations by biomarker distribution patterns. Further an upstream reference sample was investigated.

The performed fingerprinting investigations show, that the TPH pollutions in Berlin-Neukölln are gasoline contaminations. The characteristic “lubricating oil slope” of the chromatogram is recognizable in the $A_{PA}$ water sample of the former fuel depot and indicates an older contamination. Also the organic substances distributions determined in the screenings show, that a contamination exists, which is already considerably aged (biodegradation). The presented data allow a limitation of the contamination age in the area of the former fuel deposit of > 10 years. Also for the contamination in the area of the former separator a contamination age of >10 years was determined by using the time approximation algorithm for the chronological contamination limitation. The results of the lead isotope investigations showed, that the gasoline is unleaded. The determined lead isotope ratios of the samples originate from American munitions used in World War II. The concentrations of hydrocarbons in the soil gas are explicitly low. Due to the low concentrations and the presence of hydrocarbons > C1, a slow microbiological degradation must be assumed.

Having the type and the age of the pollution, the liable operator can be concluded from the ownership documents of the fuel station property.

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