Long-term impact of acid resin waste deposits on soil quality of forest areas
I. Contaminants and abiotic properties.

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1 ***Abstract***

2 Acid resins are residues characterised by elevated concentrations of hydrocarbons and heavy
3 metals, which were produced by mineral oil industries in Central Europe during the first half
4 of the last century. Due to the lack of environmental legislation at that time, these wastes were
5 dumped into excavated ponds in public areas without further protection. In this work, the
6 long-term effects of such resin deposits on soil quality of two forest areas (Bayern, Germany)
7 were assessed. We evaluated the distribution and accumulation of contaminants in the
8 surroundings of the deposits, where the waste was disposed of about 60 years ago. General
9 soil chemical properties such as pH, C, N and P content were also investigated. Chemical
10 analysis of resin waste from the deposits revealed large amounts of potential contaminants
11 such as hydrocarbons (93 g kg⁻¹), As (63 mg kg⁻¹), Cd (24 mg kg⁻¹), Cu (1835 mg kg⁻¹), Pb
12 (8100 mg kg⁻¹) and Zn (873 mg kg⁻¹). Due to the location of the deposits on a hillside and the
13 lack of adequate isolation, contaminants have been released downhill despite the solid nature
14 of the waste. Five zones were investigated in each site: the deposit, three affected zones along
15 the plume of contamination and a control zone. In affected zones, contaminants were 2 to 350
16 times higher than background levels depending on the site. In many cases, contaminants
17 exceeded the German environmental guidelines for the soil-groundwater path and action
18 levels based on extractable concentrations. Resin contamination yielded larger total C/total N
19 ratios in affected zones, but no clear effect was observed on absolute C, N and P
20 concentrations. In general, no major acidification effect was reported in affected zones.

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24 ***Keywords:*** acid resin; arsenic; heavy metals; hydrocarbons

1 ***1. Introduction***

2 Intense industrial activity and the lack of effective environmental legislation during
3 the first half of the last century gave rise to many contaminated sites all across Europe.
4 According to recent estimates the number of polluted sites lies between 300000 and 1.5
5 million (COM, 2002). Although the range of contaminants varies from country to country,
6 hydrocarbons and heavy metals have been reported overall as the main soil contaminants
7 (EEA, 2007).

8 Monitoring the accumulation and mobility of potential pollutants in natural affected
9 systems provides crucial information regarding the fate of contaminants in the environment,
10 the natural attenuation potential of soils and the long-term impact of anthropogenic
11 disturbance on soil quality (Adriano, 2001). Due to the complexity of soils, characterised by
12 multiple interactions between abiotic and biotic components, environmental studies related to
13 soil quality should consider the determination of various physical, chemical and
14 microbiological properties (Carter et al., 1999; Schlöter et al., 2003).

15 Despite many dump sites being co-contaminated with hydrocarbons and heavy metals,
16 there are very few studies, where the distribution of these groups of contaminants and their
17 effects on soil quality have been addressed in a long-time perspective (Gianfreda et al., 2005;
18 Adesodun and Mbagwu, 2008). Remediation of sites showing multiple contaminations is
19 mainly constrained by their complexity and the economic aspect (who should pay and how
20 much). In such cases, reliance on natural attenuation mechanisms may be a suitable option for
21 some areas, depending on site specific risks and end use (Werner et al., 2004). However,
22 current knowledge of such systems is rather limited generally resulting in abandonment or
23 remediation failure.

24 Good examples of multi-contaminations are sites where acid resins have been dumped.
25 These are residues that were produced by mineral oil facilities in Central Europe during the
26 first half of the last century. Such wastes were generated during the recycling of used oils by

1 the Benzmann process, in which used oils were extracted with concentrated sulphuric acid
2 and then filtered over bleaching clay (Kloos et al., 2006). The filtrate was further processed
3 for reuse, whereas the residue (acid resin) was generally mixed with rubber to improve
4 solidification. Resins were very acidic and enriched with hydrocarbons and heavy metals,
5 mainly Pb. Without further isolation or sealing, wastes were commonly dumped into
6 excavated ponds in forests or other enclaves. Although there is no official inventory of such
7 sites, estimations based on the number of active mineral oil factories at that time (between 20-
8 40) and a mean of 2-4 dumping sites per factory suggest a total of 40-160 resin contaminated
9 sites in Germany alone.

10 The present study was designed to evaluate the environmental risk of acid resin
11 deposits on soil quality of two forest areas, where the resin had been disposed of about 60
12 years ago. In this work, we investigated the release and accumulation of hydrocarbons,
13 arsenic and heavy metals in topsoil from the surroundings of the deposits and compared the
14 obtained results with the German environmental guidelines for soils. The study was focused
15 on this depth because: a) this layer poses a higher risk than the subsoil for contaminant entry
16 in the food chain (f.ex. fungi and deer), b) it implies a direct contaminant exposure to
17 organisms and humans and c) soil microbial and biological activity related to organic matter
18 turnover and nutrient cycling takes place mainly here. To gain a better insight into the abiotic
19 environment of such contaminated areas additional properties related to soil chemistry and
20 fertility such as pH, C, N and P contents were also studied. Results reported here may be
21 relevant to the environmental protection of other sites with similar contamination sources.

22 23 **2. Material and methods**

24 *2.1. Site description*

1 The two sites are located near the city of Kronach (Bayern, Germany). Their
2 coordinates are N 50°13' latitude and O 11°19' longitude for site A (Schlangenburg) and N
3 50°14' latitude and O 11°18' longitude for site B (Seelacher Berg). They are both situated on
4 a hilly landscape (about 320m high), which mainly consists of mixed forest dominated by
5 *Picea abies* (L.) Karst, *Fagus sylvatica* L. and *Pinus sylvestris* L. in Schlangenburg (site A),
6 and *Fagus sylvatica* L., *Coryllus avellana* L., and to a lesser extent *Pinus sylvestris* L., *Populus*
7 *tremula* L. and *Picea abies* (L.) Karst. in Seelacher Berg (site B). The climate lies between
8 oceanic and continental (Foken, 2007) with mean annual temperature of 8°C and mean annual
9 precipitation of 765mm. The soils were classified as loamy sand (site A; 85% sand, 14% silt
10 and 1% clay) and sandy loam (site B; 77% sand, 16% silt and 7% clay).

11

12 2.2. Soil sampling

13 The sites were surveyed at the end of October 2006. The investigated areas comprised
14 approximately 5600m² (Schlangenburg) and 4800m² (Seelacher Berg) (Figure 1). The total
15 volume of the deposits is around 900-1000m³ in Schlangenburg and 1000-1200m³ in
16 Seelacher Berg. At each site five zones were investigated: i) the deposit, where the acid resin
17 was disposed of (D), ii) a control zone unaffected by the waste and therefore not contaminated
18 (C) and iii) three zones along the plume of contamination (X) (Figure 1). The direction of the
19 contamination plume at the surface level was previously determined in June 2006 via an
20 exploratory survey. A stratified sampling was chosen because of the irregular distribution of
21 the contamination at surface level, particularly in site A (Schlangenburg). The relative
22 position of each zone from the deposit is indicated in Figure 1.

23 Within each selected zone (deposit, control or contaminated) five independent samples
24 were collected in an area of approximately 20m². Every sample was in turn a composite
25 mixture of 15-20 soil cores (0-15cm depth). Since the study focused on long-term

contamination effects, the litter layer was excluded to avoid the influence of recently added material to the soil system. No vegetation was directly growing on the surface of sampled zones, but woody species in both areas showed no apparent signs of toxicity.

Transport to the laboratory was achieved within 3 hours after the sampling. For assessment of gravimetric water content, water holding capacity and total hydrocarbons soil subsamples were stored at 4°C until analysis (within 3 weeks after the sampling). For determination of the other chemical properties, soil samples were dried for 4 days at room temperature.

2.3. Physical and chemical properties

Soil texture was determined by the method of Gee and Bauder (1986). The gravimetric water content and the water holding capacity (WHC) were determined as described by Forster (1995). Soil pH was measured in 1/5 sample/0.01M CaCl₂ (v:v) extracts as reported in DIN ISO 10390.

The total organic C (TOC) and total N content (TN) were determined after combustion of solid-phase samples using an elemental analyser Eurovector CN coupled with a gas chromatograph/isotope ratio mass spectrometer (GC/IRMS) (Finnigan MAT DeltaPlus, Bremen, Germany).

Extractable C (Ex-C) and Extractable N (Ex-N) were obtained using 1/4 soil/0.01M CaCl₂ solution extracts after shaking on an over-head shaker for 15min and subsequent filtration of extracts through 0.4µm pore diameter Nucleopore polycarbonate Track-Etch Membrane (Whatman). Total C and N concentrations in the extracts were determined via catalytic high temperature oxidation using a TC/TN DIMATOC Analyzer (Dimatec Analysentechnik GmbH, Germany) (Zsolnay, 2003).

Extractable-P (Ex-P) was determined in 1/20 soil/0.1N NaHCO₃ extracts (Olsen et al., 1954) by the colorimetric procedure of Murphy and Riley (1962) using an automated continuous flow analyzer (Bran + Luebbe III; Germany).

2.4. Total hydrocarbons

Total hydrocarbon concentrations in soil were determined by means of GC-MS (gas chromatography-mass spectrometry). The extraction procedure was the same as described in DIN ISO 16703. The recovery of standards after solid phase purification was 100%. Purification was carried out using BondElute LKC-FL cartridges containing 500mg of Florisil (VarianInc, The Netherlands). The purified extracts (hexane) containing the hydrocarbons (10mL) were evaporated and re-diluted in isooctane (200μL) and then injected (splitless mode) in the GC system (GC Trace, Thermo Finnigan) equipped with a capillary column (BP5 SGE; 60m x 0.25mm i.d.). The area comprised between the decane and tetracontane peaks was integrated using the X-calibur™ software (Thermo Finnigan, San Diego, CA, US) to calculate the total concentration of hydrocarbons.

2.5. Total and extractable As, S and heavy metals

Total As, S and metal concentrations in soil (<60μm) were determined via ICP-OES (Inductively coupled plasma-optical emission spectrometry) using a IRIS ADVANTAGE spectrometer (Thermo Jarrel Ash Corporation, MA, US) after *aqua regia* microwave assisted digestion (Microwave Laboratory Station Milestone ETHOS 900, Milestone s.r.l., Sorisole, Italy). Accuracy was routinely checked by reference to digests of standard reference soils (CRM 141 and CRM 277) (Table 1). Soil 0.01M CaCl₂-extractable trace element concentrations were determined using 1/10 soil sample (<2 mm)/0.01 M CaCl₂ extracts via

ICP-OES (Ure et al., 1993). The detection limits of the method used were: As=0.1mg kg⁻¹, Cd=0.01mg kg⁻¹, Cu=0.05mg kg⁻¹, Pb=0.1mg kg⁻¹, Zn=0.01mg kg⁻¹.

2.6. Statistical analysis

A normality test was carried out for all variables prior to analysis of the variance. ANOVA tests were performed for differences between values of contaminants and chemical properties, considering the zone as the independent variable. Statistically significant differences were established by Tukey's test when there was homogeneity of the variance and by Games-Howell's test when there was not. Correlations between contaminant-related and chemical properties for each site were also performed. The significance level reported ($p<0.01$ and $p<0.05$) was based on Pearson's coefficients. Correlations were performed separately for each site as combining the two datasets changed some of the local interdependencies. In order to evaluate the interactions of contaminants with abiotic soil properties, deposits were excluded. The inclusion of the latter significantly influenced results in both sites (data not shown).

3. Results & Discussion

3.1. Soil pH

Values of pH in deposit samples were found to be particularly low (around 1.5 units) (Table 1). Given the extreme acidic nature of the resin one of our major goals was to find out if changes in soil pH had occurred around the deposit. It is known that hydrocarbon degradation is optimal at neutral pH (USEPA, 2006) and heavy metal solubility favoured at low pH (Adriano, 2001). Therefore acidification of surrounding areas could negatively affect the natural attenuation potential of the soil and enhance metal mobility. Despite the low pH of the resin, there were no clear acidification effects outside deposit A with the exception of the

1 most adjacent area, X_{A1} in which a pH value of 2.5 was recorded (Table 1). In the other
2 sampled zones, pH values were also relatively low (around 3), suggesting that the soil of site
3 A was naturally acid. This may be attributed to a combination of the following factors i) the
4 nature of the parent material, typical sandstone rich in silicates with low Ca and Mg content,
5 ii) the climate of the area, cold and moderately humid, and iii) the accumulation of organic
6 matter from plant material (basically needles). In addition, long-term effects of S and N
7 deposition on sandy forests may have enhanced soil acidification processes (Lückewille and
8 van Breemen 1992; Meesenburg et al., 1995). In site B, pH values were generally less acidic
9 than in site A, which may be due to differences in clay content between the two sites (around
10 6% more clay) and organic matter quality (more abundance of deciduous leaves) (Rothe et al.,
11 2002). Local heterogeneity was also higher in site B, with pH differences up to 2 units (Table
12 2). In some of the contaminated zones (X_{B2} and X_{B3}) pH was even higher than in the control
13 zone, hence no evident acidification effects could be ascribed to the resin in those zones.
14

15 3.2. Total and extractable C, N and P

16 The composition of the resin, enriched with hydrocarbons, resulted in elevated
17 concentrations of organic C in the deposits (around 55%) (Table 2). As a consequence, it
18 would be expected that alterations of the organic C pool in contaminated zones might occur.
19 In site A, total C concentrations in contaminated zones of site A were lower than those found
20 in the control area, whereas in site B total C concentrations were larger in contaminated zones
21 than in the control (Table 2). Therefore differences in C content outside the deposits could not
22 be solely attributed to hydrocarbon contamination and were probably highly influenced by
23 local organic matter accumulation patterns. Since it was not possible to discriminate between
24 resin-derived and natural C, interpretations about total C concentrations should be taken with
25 caution. Nonetheless, we were interest on this parameter to evaluate possible interactions

1 between the C pool, metals and biological properties (see also Pérez de Mora et al., in press
2 for the latter).

3 In contrast to C, nitrogen was not a major component of the resin (only 2.8% of the dry
4 matter) (Table 2) and thus no resin effect on the N pool was expected outside the deposits.
5 Total N concentrations in affected zones and controls followed a similar trend as that
6 observed for total C, as the positive correlations between these two variables indicate (Tables
7 3 and 4). Therefore, differences in N concentrations between zones were also probably related
8 to differing natural organic matter content rather than accumulation of contaminants.

9 Significant differences were observed in the total organic C to total N ratio between the
10 deposits, contaminated zones and the control area (Table 2). Larger C/N ratios were observed
11 in affected zones compared to the controls; particularly in the deposits (Table 1). Although an
12 increase of the C/N ratio in contaminated zones could be also influenced by differences in the
13 quality of the organic matter present in each particular zone, a similar effect has been reported
14 in other studies involving oil spills (Hoyle et al., 1995; Hupe et al., 2001). In line with this,
15 there was a high positive correlation between the C/N ratio and hydrocarbon concentrations in
16 both sites (Table 3 and 4), as opposed to total C and N concentrations.

17 Dissolved organic C influences soil biology and chemistry, and represents the labile C
18 pool which stimulates microbial activity in soil (Caravaca and Roldán, 2003; García et al.,
19 2005). At the same time, dissolved organic compounds can act as solvents or quelating agents
20 for other relatively insoluble organic compounds and heavy metals, enhancing the mobility of
21 contaminants (Kördel et al., 1999). In both deposits, concentrations of extractable C were
22 higher than in the other zones, suggesting the presence of soluble hydrocarbon compounds in
23 the resin (Table 2). Nonetheless, this fraction only accounted for 1/1000 (site A) and 1/600
24 (site B) of the total C pool. In site A, extractable C concentrations were higher in the control
25 area and X_{A1} than in the other contaminated zones, whereas in site B similar or even higher
26 concentrations were observed in the control area compared to contaminated zones (Table 2).

1 As a result, concentrations outside the deposits did not seem to be influenced by the
2 contamination (Table 2) and might be related to other site characteristics and processes such
3 as the amount and nature of total organic C (site A, Table 2), the mineralization of organic
4 matter by soil microorganisms (Kaiser et al., 2002) or the association of soluble organic
5 compounds with hydrophobic organic pollutants (Raber and Kögel-Knabner, 1997).

6 Extractable N showed a similar pattern to dissolved organic C. The highest values were
7 recorded in the deposits, but control areas showed similar or even higher concentrations than
8 contaminated zones in both sites (Table 2). Therefore there was no evident resin effect on the
9 labile N pool outside the deposits and, as it was suggested for extractable C, site-specific
10 microbiological and chemical processes may account for local differences in N extractability.
11 The EC/EN ratio was around 10 in all areas (Table 2), including the deposits, and hence no
12 evidence of shifts in labile C and N pools due to the contamination could be obtained from
13 this ratio. Like nitrogen, phosphorus was not a major component of the resin and, although the
14 highest concentrations were found in contaminated zones of both sites, P extractability was
15 lower in the deposits compared to the surroundings (Table 2).

17 3.3. *Hydrocarbons*

18 Concentrations of hydrocarbons in the acid resin of the deposits were equivalent to
19 approximately 1000 times those found in control areas (Figure 2). The severity of the
20 contamination was also patent in the contaminated zones of both sites, where hydrocarbon
21 concentrations were between 3-150 times higher in site A and 16-350 times higher in site B
22 than those found in controls (Figure 2). These results clearly show that hydrocarbons have
23 been released from the deposits over the last 60 years despite the hydrophobic and solid
24 nature of the resin. In addition, there were inherent differences in the hydrocarbon
25 accumulation pattern along the plume between both sites in spite of the similar composition of
26 the resin. In site A, hydrocarbon content was highest in an intermediary zone (X_{A2}) of the

1 plume, whereas in site B mean concentrations were highest in the closest zone to the deposit
2 (X_{B1}) and decreased as distance from the deposit increased (Figure 2). Studies from
3 contaminated areas have frequently shown that the spatial distribution of contaminants is
4 often irregular, even at short distances, due to the accidental nature of the contaminant process
5 and soil heterogeneity (Carlon et al., 2001; Burgos et al., 2006). As it can be inferred from
6 Figure 1, the two sites have distinct topological characteristics. In site A, there is a drastic
7 change in slope between the zone adjacent to the deposit (X_{A1}) and the intermediary zone X_{A2}
8 (Figure 1a), whereas in site B the topological profile is more continuous (Figure 1b). In
9 addition, lower clay content and natural organic matter in affected zones of site A could result
10 in low contaminant retention (Litz et al, 2004). Interestingly, this phenomenon was observed
11 for hydrocarbons but not for heavy metals (section 3.5). This could be also due to the nature
12 of non-polar hydrocarbons, which are less reactive and hence less efficiently immobilised by
13 the soil matrix than polar compounds or inorganic elements (Grathwohl, 1997). Long-term
14 exposure to the resin has resulted in the accumulation of hydrocarbons in all contaminated
15 areas to concentrations which exceed the investigation threshold (200mg kg^{-1}) proposed for
16 the soil-groundwater path by the German environmental guidelines (BBodSchG, 1998). In
17 addition, mean concentrations in contaminated zones X_{A1} , X_{A2} and X_{B1} exceeded the
18 intervention limit for soils of 5000mg kg^{-1} established by other European countries (VROM,
19 2000). At present there are no intervention levels in Germany based on total hydrocarbons.

20

21 3.4. Total As, S and heavy metals

22 Heavy metals are frequently found together with hydrocarbons in spills of used oils
23 (Adeyini and Alofabi 2002; Muniz et al., 2004). Analysis from deposit samples showed that
24 in addition to hydrocarbons and S derived from the use of H_2SO_4 in the recycling process,
25 moderately to high concentrations of As, Cd, Cu, Pb and Zn were present in the resin (Figure
26 3). In contrast to hydrocarbons and S, concentrations of As and heavy metals differed between

1 the two deposits: with the exception of Zn, trace elements in deposit B were twice than in
2 deposit A (Figure 3). In site A, significant differences between contaminated and control
3 zones were only recorded in X_{A1} , in which Pb and S concentrations were 5 and 4 times higher,
4 respectively, than those found in the control area (Figures 3d and e). In site B, total
5 concentrations of most elements were significantly higher in contaminated zones compared to
6 the control area (Figure 3). Concentrations of As, Cd and Cu were around 2-16 fold higher in
7 contaminated zones than those observed in the control (Figures 3a, b and c). In the case of Pb
8 and the control element S differences were even larger (7-140 times for Pb and 3.5-26 times
9 for S) (Figures 3d and e), whereas mean values of Zn were only 2-2.7 fold higher than
10 background levels of the control area (Figure 3f). The extent of the contamination was
11 therefore larger in site B than in site A and concentrations of the studied elements generally
12 exceeded the investigation threshold for the soil-groundwater path established by the German
13 law (Table 5). In site A, this situation only occurred for Pb in zone X_{A1} .

14

15 3.5. Extractable As, S and heavy metals

16 Based on previous experiences, we decided to use a 0.01M CaCl_2 -based extraction to
17 assess the potential bioavailability of trace elements in soil. In general, the highest
18 concentrations were recorded in the deposits (Figure 4). In site A, extractability of all
19 elements, except As, was significantly higher in X_{A1} compared to the control area (Figure 4).
20 For the other contaminated zones no significant differences were found. In site B, the main
21 differences between contaminated and control zones were also observed for the closest area to
22 the deposit (X_{B1}). Here, extractable concentrations of As, Pb and Zn were approx. 17 fold
23 higher than in the control area (Figures 4a, d and f). In the case of Cu and S, differences of 64
24 and 80 fold, respectively, were observed (Figures 4c and e). Differences between the control
25 zone and X_{B2} were also reported for S and Zn (Figures 4e and f). Results indicate that the
26 extractability of trace elements was highly related to their total concentrations (Tables 3 and

4), as it has been reported in other contaminated areas, in which the spatial distribution of contaminants resulted from remains of the waste material (Burgos et al., 2006). In line with other studies assessing metal solubility (Naidu et al., 2001; Adriano et al., 2004), extractability of all cationic elements was negatively correlated with soil pH in both sites (Tables 3 and 4). Metal extractability was also positively correlated with extractable C and N concentrations in site A, while in site B this trend was observed for total organic C and total N (Tables 3 and 4). Heavy metals and trace elements generally show high affinity for soil organic matter due to its numerous functional groups capable of binding inorganic elements (Harter and Naidu, 1995). In turn, enhanced mobility of metals via complexation to soluble organic matter may also occur (Ross, 1994). This could be the case in zones C_A and X_{A1}, where concentrations of DC and DN were much larger than in the other zones (Table 1).

Although legislation does not consider extractable concentrations for environmental risk assessment yet, Prueb (1997) proposed intervention values for German soils based on 1M NH₄NO₃ extraction (DIN 19730). Despite using a milder extraction procedure, we found concentrations of As and heavy metals in X_{A1} and X_{B1}, and Cd, Cu and Zn in X_{B2}, above the threshold proposed by Prueb (1997) (Table 5). As it has been reported in other areas contaminated with As and the same four metals (Pérez-de-Mora et al., 2007), the relative mobility, that is the [Metal]_{soluble}/ [Metal]_{total} ratio, of Cd and Zn was higher than that of the other contaminants (data not shown). Such result can be attributed to the different behaviour of these elements in soils. Copper and lead can generally bind better to soil organic matter than other metals and thus may show restricted solubility in topsoil (Al Chalabi and Hawker 2000; Xiandong et al., 2001). Due to its anionic nature arsenic is less mobile under acid than alkaline conditions (Adriano 2001), whilst cadmium and zinc have been reported to be relatively mobile compared to other metals (Basta et al., 2005; Kabata-Pendias, 2001). The latter elements could therefore leach more easily to groundwater or enter the food chain compared to other major constituents of the resin such as Cu or Pb. Future research should

1 consider a more restrictive sampling at deeper depths to follow contaminant movement down
2 the soil profile, particularly in the case of hydrocarbons due to their non-polar character.

4 **4. Conclusions**

5 We could show that over the past 60 years hydrocarbons, arsenic and metals have been
6 released from the studied deposits. Acid resin deposits can therefore act as contamination
7 sources for the environment despite the hydrophobic and solid nature of such residues. In
8 many cases, contaminants have accumulated to extents that exceed the investigation levels for
9 the soil-groundwater path proposed by the German legislation and action levels based on mild
10 extraction procedures. As a consequence the fate of such contaminants should be monitored in
11 the long-term and concentrations in groundwater controlled. Despite the acidity of the resin,
12 no major effect on soil pH was observed in the surroundings, which was naturally acid. In
13 relation to the cycling of nutrients, acid resin contaminations can widely alter the total C/total
14 N ratio in the soil while not showing a clear effect on absolute C, N and P values.

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1 **Caption of figures**

2 Figure 1. 3D View of site a) Schlangenburg and b) Seelacher Berg with sampling zones
3 included. C = control; D = deposit; Horz. = horizontal distance; Vert. = vertical distance; X =
4 contaminated zone. ••••• Limit of deposit.

5
6 Figure 2. Mean values and standard errors of total hydrocarbons. Columns with the same
7 letter do not differ significantly, $P < 0.01$.

8
9 Figure 3. Mean values and standard errors of total concentrations of a) arsenic, b) cadmium,
10 c) copper, d) lead, e) sulphur and f) zinc. Columns with the same letter do not differ
11 significantly, $P < 0.01$.

12
13 Figure 4. Mean values and standard errors of extractable concentrations of a) arsenic, b)
14 cadmium, c) copper, d) lead, e) sulphur and f) zinc. Columns with the same letter do not differ
15 significantly, $P < 0.01$.

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17
18

Figure 1

Figure 2

Figure 3

Figure 4

Table 1. Analysis of BCR samples (n = 6). Mean values are given in mg kg⁻¹.

Element	CRM 144				CRM 277			
	Certified		Experimental		Certified		Experimental	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
As	(8)	ND	7.19	1.14	47.3	1.61	43.8	0.69
Cd	0.36	0.10	0.42	0.06	11.9	4.05	10.7	0.16
Cu	32.6	1.40	35.6	2.47	43.4	1.60	45.6	1.84
Pb	29.4	2.58	31.2	1.23	146	3.07	143	1.53
Zn	81.3	3.5	78.2	3.14	547	12.0	541	4.02

(Indicative); ND = not determined; SD = standard deviation.

Table 2. Mean values of general soil physical and chemical properties of each zone.

	WHC (g 100g ⁻¹)	pH	TOC (g kg ⁻¹)	TN (g kg ⁻¹)	C/N	Ex-C (mg kg ⁻¹)	Ex-N (mg kg ⁻¹)	DOC/TDN	Ex-P (mg kg ⁻¹)
Site A (Schlangenburg)									
C_A	67.5 a	2.97 c	74.8 b	3.45 b	21.8 a	319 b	25.5 b	12.5 b	13.9 a
D_A	100 c	1.55 a	570 c	2.87 b	199 c	445 c	51.0 c	8.72 a	39.4 b
X_{A1}	71.1 ab	2.52 b	66.1 ab	1.34 a	49.0 b	281 b	19.8 ab	12.3 ab	53.0 b
X_{A2}	82.9 b	3.32 c	34.8 ab	0.67 a	53.1 b	68.6 a	5.55 a	12.2 ab	86.5 bc
X_{A3}	77.6 b	3.20 c	27.1 a	1.19 a	20.9 a	71.7 a	7.95 a	9.17 ab	108 c
Site B (Seelacher berg)									
C_B	69.2 a	3.31 b	30.5 a	2.12 a	14.4 a	222 b	23.8 a	9.45 b	41.9 b
D_B	100 c	1.37 a	520 c	2.73 ab	193 c	890 c	88.4 b	10.3 b	4.19 a
X_{B1}	87.6 b	3.31 b	340 bc	7.84 c	45.9 b	175 ab	20.2 a	8.93 ab	71.3 bc
X_{B2}	80.7 b	4.22 bc	76.2 b	3.75 b	20.3 ab	191 b	23.5 a	8.26 ab	67.1 c
X_{B3}	69.2 a	5.30 c	78.5 b	3.44 ab	23.5 a	95.2 a	18.3 a	5.61 a	74.8 c

C = control zone; D = deposit; Ex = extractable; TN = total N; TOC = total organic C; WHC = water holding capacity; X = contaminated zone. Values followed by the same letter do not differ significantly ($P \leq 0.01$).

Table 3. Pearson's correlations for site A (n = 20).

	pH	TOC	TN	Ex-C	Ex-N	Ex-P	HC	As	Cd	Cu	Pb	S	Zn	Ex-As	Ex-Cd	Ex-Cu	Ex-Pb	Ex-S	Ex-Zn
pH	1	-.627**	-.225	-.804**	-.769**	.329	.088	.264	.216	-.257	-.902**	-.874**	-.764**	.179	-.817**	-.828*	-.930**	-.851**	-.882**
TOC		1	.769**	.755**	.778**	-.408	-.078	.064	-.207	.017	.483*	.484*	.536*	-.161	.459*	.395	.452*	.412	.490*
TN			1	.529*	.640**	-.380	-.434	.343	.012	.031	-.010	-.030	.300	-.207	-.001	-.055	-.072	-.056	.033
Ex-C				1	.971**	-.433	-.100	-.084	-.150	.163	.616**	.721*	.766**	-.162	.817**	.781**	.611**	.776**	.827**
Ex-N					1	-.543*	-.197	-.093	-.188	.105	.543*	.599*	.698**	-.162	.690**	.661**	.533*	.655**	.716**
Ex-P						1	-.039	.645**	.750**	.432	-.165	.001	-.043	.043	-.177	-.120	-.164	-.106	-.195
HC							1	-.377	-.286	-.287	.014	.151	-.206	.189	.192	.149	.089	.163	.125
As								1	.894**	.605**	-.273	-.118	.243	-.134	-.244	-.222	-.345	-.229	-.231
Cd									1	.743**	-.184	.018	.316	-.065	-.124	-.046	-.234	-.064	-.108
Cu										1	.264	.364	.684**	-.262	.234	.322	.198	.298	.289
Pb											1	.891**	.704**	-.162	.746**	.776**	.940**	.794**	.810**
S												1	.807**	-.078	.917**	.943**	.909**	.957**	.946**
Zn													1	-.248	.760**	.796**	.655**	.778**	.817**
Ex-As														1	-.059	-.073	-.127	-.063	-.094
Ex-Cd															1	.974**	.810**	.977**	.983*
Ex-Cu																1	.825**	.994**	.983**
Ex-Pb																	1	.863**	.868**
Ex-S																		1	.988**
Ex-Zn																			1

Ex = extractable ; HC = total hydrocarbon content; TN = total dissolved N; TOC = total organic C. * $P \leq 0.05$; ** $P \leq 0.01$.

Table 4. Pearson's correlations for site B (n = 20).

	pH	TOC	TN	Ex-C	Ex-N	Ex-P	HC	As	Cd	Cu	Pb	S	Zn	Ex-As	Ex-Cd	Ex-Cu	Ex-Pb	Ex-S	Ex-Zn
pH	1	-.301	-.090	-.579**	-.016	.542*	-.350	-.268	.048	-.353	-.350	-.377	.014	-.443	-.619**	-.457*	-.592**	-.559*	-.553*
TOC		1	.766**	-.201	-.408	.057	.916**	.761**	.331	.966**	.935**	.992**	.328	.475*	.539*	.349	.677**	.603**	.562**
TN			1	-.015	-.024	.474*	.455*	.920**	.712**	.614**	.510*	.718**	.701*	.559*	.562**	.434	.554*	.639**	.621**
Ex-C				1	.685**	-.260	-.244	.003	.007	-.211	-.229	-.168	.024	.275	.290	.419	.241	.260	.216
Ex-N					1	.254	-.513*	-.104	.039	-.489*	-.513*	-.416	.061	.163	.019	.279	.025	.042	-.026
Ex-P						1	-.223	.399	.491*	-.138	-.215	-.012	.318	.248	.117	.120	.089	.192	.167
HC							1	.465*	.022	.972**	.994**	.933**	.027	.273	.384	.222	.586**	.421	.368
As								1	.725**	.615**	.511*	.749**	.689**	.754**	.736**	.519*	.640**	.796**	.817**
Cd									1	.236	.098	.305	.917**	.328	.513*	.185	.096	.469*	.622**
Cu										1	.988**	.974**	.246	.323	.472*	.256	.592**	.500*	.477*
Pb											1	.949**	.113	.274	.405	.229	.575**	.443	.396
S												1	.297	.508*	.591**	.394	.708**	.649**	.605**
Zn													1	.241	.357	.080	.013	.343	.487*
Ex-As														1	.791**	.742**	.753**	.874**	.830**
Ex-Cd															1	.777**	.784**	.957**	.964**
Ex-Cu																1	.839**	.817**	.650**
Ex-Pb																	1	.841**	.679**
Ex-S																		1	.936**
Ex-Zn																			1

Ex = extractable ; HC = total hydrocarbon content; TN = total dissolved N; TOC = total organic C. * $P \leq 0.05$; ** $P \leq 0.01$.

Table 5. Arsenic and heavy metal reference values for Germany

	Investigation threshold for the soil-groundwater path (mg kg⁻¹)^a	Intervention threshold based on 1M NH₄NO₃ extraction (mg kg⁻¹)^b
As	10	0.1
Cd	5	0.08
Cu	50	1
Pb	25	3
Zn	500	5

^aBBodSchG (1998); ^bPrueb (1997)