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**The influence of soil organic matter (SOM) on the accumulation and transformation of inorganic and organic pollutants**

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# **The influence of soil organic matter (SOM) on the accumulation and transformation of inorganic and organic pollutants**

## **INTAS - Project**

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## **Final Report**

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## SUMMARY

**Title:** „The influence of soil organic matter (SOM) on the accumulation and transformation of inorganic and organic pollutants“

**Ref. No.:** INTAS-93-1168

**Project co-ordinator:** UFZ Centre for Environmental Research Leipzig-Halle  
Department Soil Sciences

**Duration:** 17 months

Soil organic matter greatly influences the mobility and bio-availability of nutrients and pollutants and determines their risk of being transported to deeper soil layers and aquifers or of plant uptake. The task of this project was the estimation of the mobility and availability of inorganic and organic pollutants of soils and the investigation of the role of SOM in these processes. Poorly understood is especially the kind of linkages of pollutants with humic substances and clay minerals which determine the stability of the formed complexes. Using two in principle completely different methods of SOM fractionation a) a very easily decomposable fraction of SOM which correlates to soil biological parameters was isolated by a hot water extraction. b) For determining the linkages of SOM and pollutants to soil particles, especially to clay minerals, a granulodensimetric fractionation was done. Within the project work two analytical methods were developed as a supposition for the determination of organic pollutants: a) in the hot water fraction of SOM and b) in very small samples (50 to 100 mg) of the granulodensimetric fractions of SOM. Soils from sites in Germany, Russia and North Bohemia differing in their contamination degree with heavy metals and organic pollutants were investigated using specific methods of the participants. In the hot water extracts and granulodensimetric fractions of soils the distribution of SOM, heavy metals and selected organo-chemicals (chlorinated hydrocarbons, polycyclic aromatic hydrocarbons) was determined. The influence of these substances on soil microbial biomass and their activities was investigated using various methods. The determination of the contents of heavy metals and organo-chemicals, especially  $\beta$ -HCH, in the hot water extractable fraction of soil organic matter seems to be one possibility for an evaluation of the behaviour (mobility and bio-availability) of inorganic and organic pollutants in soil.



## 1. INTRODUCTION

This report represents the co-operative work of three groups of scientists participating in the INTAS-funded project INTAS-93-1168.

The duration of the project was 17 months including an extension of 3 months.

## 2. OBJECTIVES OF THE PROJECT

Main task of the project was the evaluation of the role of Soil Organic Matter (SOM) in the estimation of soil contamination and its risks for other environmental compartments. As indicated in the work programme polluted soils were selected to evaluate the mobility of pollutants in soil with specific objectives:

- determination of mobile fractions of pollutants using various extractants
- determination of pollutants in fractions of SOM with low stability to a microbial degradation (bioavailability)
- determination of the linkage of nutrients and pollutants to SOM using a physical fractionation of the soil corresponding to the particle size and density of fractions (granulodensimetric fractionation)
- determination of the soil microbial biomass as a faktor of great influence for transformation processes in soil.

### **3. RESEARCH ACTIVITIES**

#### **3.1. DESCRIPTION**

Soil Organic Matter (SOM) influences the majority of chemical, physical and biological soil properties and soil processes, in particular, mineralization and immobilization as well as transport and plant uptake of both nutrients and pollutants. For the evaluation of the mobility and availability of these substances it is necessary to determine how they are linked to parts of SOM.

There exist a wide range of methods and aspects for a fractionation of SOM which are more or less practicable for special tasks. Principles of fractionation methods can be completely different:

A classical chemical fractionation after BREMNER or KONONOVA is connected with humus substances or/and functional groups and leads to fragments of the SOM according the extractants used. It is practicable for investigations e.g. of a chemical structure of humic substances.

Another aspect for a fractionation of SOM is the stability to microbial attack turnover rates of the different fractions. The fractionation results in the determination of active and passive parts of SOM and their role in soil transformation processes.

There are also physical methods (particle size and/or density) used for the fractionation of SOM. The advantage of these methods is that the isolated fractions were only minimal changed in their original form so that the results are close connected to real conditions.

##### **3.1.1. MATERIALS**

Participants of this project studied soils of selected areas in Germany, Russia and North Bohemia which representing both different use and different degrees of contamination.

The following sites were used for the investigations of the project:

**GERMANY****1. Wetland site**

In the wetlands of the river Mulde in the north east of Saxonia-Anhalt in the eastern part of Germany soil samples were taken at 4 sites with differing in heavy metal contamination but all showing high contents of organo chemicals because of the former industries, in particular, chemical industry. Main pollutant in the group of organo chemicals is the  $\beta$ -isomer of hexachlorocyclohexane (HCH).

The source of  $\beta$ -HCH is the former production of Lindane, the  $\gamma$ -isomer of HCH, used in different ways as pesticide and wood protection reagent. During the production process the  $\alpha$ -,  $\beta$ -,  $\delta$ - and  $\epsilon$ - HCH were formed as by-products. With the production waste water these by-products have been deposited in the river Mulde and the surrounding areas. Due to various natural flooding situations these substances were spread in the wetlands and caused a more or less contamination of soil.

Table 1 shows some selected soil parameters for the characterization of the sites.

**Tab. 1: Selected parameters for the characterization of the sites**

No.	Site	Soil and flooding	Use	pH (CaCl <sub>2</sub> )	Total C (%)	Total N (%)	C/N ratio
1	Spittelgraben (SPI) (0-30 cm)	sandy wetland soil; often flooded	without (protected area)	3,3	14,7	0,48	30,6
2	Jessnitz/Keller (KEL) (0-30 cm)	sandy-loamy wetland soil; rarely flooded	pasture for sheeps	5,4	10,34	0,63	16,4
3	Bobbau/Lange (LAN) (0-30 cm)	sandy wetland soil; very rarely flooded	pasture for sheeps	4,0	1,73	0,13	13,3
4	Greppin (GRE) (0-30 cm)	heavy loamy wetland soil; rarely flooded	pasture	6,0	3,1	0,23	13,5

## 2. Urban site of the Leipzig city

The sampled sites are located in parks of the city of Leipzig and are part of a transect across the Leipzig city. All sampled sites were of a uniform use (grasses) and they are comparable.

Some soil characteristics are given in table 2.

**Tab. 2: Characteristics of urban soils of the Leipzig city**

No.	Site	Use	Depth (cm)	Total C (%)	Total N (%)	C/N ratio	DOC (mg/l)	pH (CaCl <sub>2</sub> )
37	Mariannen Park	grass	0-10	3,97	0,30	13,3	37,5	5,5
62.1	Stephanie Platz (STE 1)	grass	0-15	1,80	0,13	13,9	15,0	6,2
62.2	Stephanie Platz (STE 1)	grass	15-30	2,41	0,16	15,1	15,9	6,4
63.1	Stephanie Platz (STE 2)	grass	0-15	1,48	0,11	13,5	14,2	6,0
63.2	Stephanie Platz (STE 2)	grass	15-30	3,35	0,24	14,0	19,2	6,6
65.1	Stephanie Platz (STE 3)	grass	0-20	1,28	0,10	12,8	14,1	5,8
65.2	Stephanie Platz (STE 3)	grass	20-40	2,94	0,19	15,5	16,0	6,5

## NORTH BOHEMIA

The region of North Bohemia near the town Chomutov belongs to the most polluted areas in Central Europe due to coal mining and power stations. Large depositions of ashes of the power stations are found which are used in combination with sewage

sludges for the cultivation of former mining places . The agricultural potential of these areas is under investigation today.

Table 3 contains selected parameters for the characterization of the sites.

**Tab. 3: Characteristics of the sites near Chomutov**

No.	Substrate	pH (CaCl <sub>2</sub> )	Total C (%)	Total N (%)	C/N ratio
5	deposite Brezno; mining substrate sewage sludge	7,4	1,80	0,15	12,0
6	deposite Brezno; mining substrate sewage sludge; ashes	6,9	3,13	0,16	19,6
7	deposite Pocerady; pure ashes; liquid sludge	7,0	2,19	0,09	24,3
8	mining substrate	4,5	4,32	0,12	36,0

Soil 5 and 6 is agricultural used. At site 7 pure ashes in combination with slurry were tested to cover the ash deposits and to establish plants against wind erosion. Soil substrate 8 is a pure deposit substrate of coal mining areas.

**INDUSTRIAL REGION NEAR MOSCOW**

**1. Site near steel mills**

In a region close to Moscow in Russia soils from agricultural used areas near steel mills were sampled upstream and downstream assuming that there are different degrees of contamination.

Table 4 contains characteristic soil parameters of the site.

**Tab. 4: Selected soil characteristics of the sites in the Moscow region**

No.	Sampling point	assumed pollution	depth (cm)	Total C (%)	Total N (%)	C/N ratio
1	1	with	2-10	2,295	0,175	13,1
2	1	without	2-10	3,908	0,327	12,0
9	1	with	13-19	0,770	0,062	12,4
10	1	without	13-19	0,256	0,036	7,1
11	1	with	50-60	0,191	0,026	7,4
12	1	without	50-60	0,149	0,025	6,0
3	2	with	2-10	4,271	0,291	14,7
4	2	without	2-10	3,697	0,306	12,1
5	3	with	2-10	3,117	0,208	15,0
6	3	without	2-10	3,323	0,266	12,5
7	4	with	2-10	4,926	0,317	15,5
8	4	without	2-10	4,734	0,374	12,7

**2. Soils from park areas, Moscow**

Soils were sampled from some park areas in the centre of the Moscow city were taken. Because of the very high traffic a pollution with polycyclic aromatic hydrocarbons was assumed.

Table 5 contains characteristic soil parameters of these sites.

**Tab. 5: Soil characteristics of samples of selected park sites in Moscow**

No.	Site	Depth (cm)	Total C (%)	Total N (%)	C/N ratio
1	Poljanka street	0-5	2,18	0,116	18,8
2	Lenin prospect	0-5	4,78	0,298	16,0
3	Kusminki park	litter	43,96	1,096	40,1
4	Kusminki park	0-5	8,32	0,395	21,1
5	Cetun (?)	litter	8,32	0,280	29,7
6	flooded soil	0-5	1,22	0,045	27,1
7	Botanical garden	0-5	4,28	0,252	17,0
8	Alexander garden	0-5	4,25	0,314	13,5

### 3.1.2. METHODS

#### 3.1.2.1. Soil characteristic parameters

- Total C - dry combustion in an oxygen stream referring to a method of STRÖHLEIN at a temperature of 1000 °C; infrared absorption of the CO<sub>2</sub> is measured
- Total N - KJELDAHL's digestion and volumetric determination of N referring to DIN 19684, Teil 4
- pH - electrometric measurement in a neutral 0,01 mol/l calcium chloride solution (VDLUFA Methodenbuch I, 1991)
- DOC - referring to DIN 38414, Teil 4 (1984), measurement with an elemental analyzer „liquiTOC“ Fa. HERAEUS

### 3.1.2.2. Heavy metals

#### Total content of heavy metals

RFA - X-Ray fluorescence analysis (wave-length dispersive, apparatus ) of the total content of heavy metals and arsenic (LAGA 1991) without destroying the sample (**Germany**)

RFA - X-ray fluorescence (energy dispersive, apparatus TEFA-G 111, USA) analysis of the total content of chromium, nickel, manganese, copper, zinc and lead (BOL'SHAKOV et.al. 1993) (**Russia**)

A nitric acid digestion (1%, v/v) using ultrasonic energy (22 KHZ; 0,5 hours) referring to LERNER et.al. (1993) was performed in **Russia**.

Aqua Regia digestion of the soil samples were done referring to DIN 38414, Teil 7 (1983) (**Germany**)

or according to McGRATH and CUNLIFFE (1985) (**Great Britain**)

to measure the following elements by:

AAS - Atomic Adsorption Spectrometry (PERKIN ELMER Zeeman AAS with graphit cuvettes) for cadmium (**Germany**) and (**Russia**)  
sample injection as a fine dispersive suspension after ultrasonic treatment referring KACHNOVICH & EPIFANOVA (1994) (**Russia**)

ICP - Atomic Emission Spectrometry of an induced coupled plasma (SPECTROFLAME) (**Germany**), (FISONS ICP-AES) (**Great Britain**)

#### Soluble and available content of heavy metals respectively

1. Extraction with ammonium nitrate solution ( $\text{NH}_4\text{NO}_3$  1 mol/l) referring DIN 19730, Teil 5 (1993)  
measurement of the heavy metals like described above
2. Extraction with hot water (BEHM 1988); extraction ratio soil/water 1:5; boiling of the soil/water mixture under reflux for one hour; aliquotes of the centrifugate are used for determination of heavy metals; measurement of the heavy metals like described above

### 3.1.2.3. Organo chemicals

#### **Extraction of polycyclic aromatic hydrocarbons (PAH) from soils**

A cold extraction method after KAMPE et.al. (1986) was used.

10 g of soil and 150 ml of a petrolether-/acetone mixture (1:2, v/v) were shaken in a rotating machine for 16 hours. The filtered raw extract was cleaned by a liquid/liquid distribution using n-hexane two times. The solvent of the combined organic phases was confined to 2 ml under vacuum at a temperature of 30 °C; remaining solvent was evaporated in a nitrogen stream. Residuals were filled up to 1-2 ml with either acetonitrile or toluene for measuring in HPLC, GC-ECD and/or GC-MSD.

#### **Extraction of chlorinated hydrocarbons (CHC) from soils**

A Soxhlett extraction method of CHC from soils was used.

10 g soil were extracted with 100-150 ml of n-hexane in a Soxhlett extractor for 4 hours. The clean up of the confined raw extract (3-4 ml) was performed with column chromatography (KAMPE et.al. 1986 modified) using Kieselgel 60 (MERCK), 10% deactivated with deionized water. A complete elution of the CHC occurred using a stepwise elution with 50 ml petrolether/dichloromethane (4:1,v/v) and 50 ml of toluene (THIER & FREHSE 1986).

Eluates were confined under vacuum to 3 ml; remaining solvent was evaporated with a nitrogen stream. Residuals were filled up to 1-5 ml of isooctane and measured with GC-ECD and/or GC-MSD.

#### **Extraction of chlorinated hydrocarbons (CHC) from hot water extracts**

The **new methodology** for determining CHC in the hot water fraction **has been worked out in CER Leipzig-Halle**. With an aliquot of the hot water extract of soils a liquid/liquid distribution using dichloromethane was done (extraction ratio 2:1, v/v). The combined organic phases were dried over sodium sulphate for 2 hours. The extracts were confined under vacuum to 2 ml at a temperature of 30 °C; remaining solvent was evaporated in a nitrogen stream. Residuals were filled up to 1 ml with toluene and measured in GC-ECD and/or GC-MSD.

### High Performance Liquid Chromatography (HPLC)

A binary high pressure gradient system Fa. KONTRON INSTRUMENTS with helium degasser system for the solvents acetonitrile and deionized water (HPLC quality both) was used to quantify the PAH. Substances were detected by a wave-length controlled fluorescence detector (SFM 625 Fa. KONTRON INSTRUMENTS). Chromatographic conditions are shown in Table 6.

**Tab. 6: Chromatographic conditions of HPLC for PAH**

column	Ultra-Sep-ES PAH 6 $\mu$ m 125 x 3 mm (Fa. SEPSERV) RP-18		
pre-column	Ultra-Sep-ES PAH 6 $\mu$ m 10 x 2 mm (Fa. SEPSERV) RP-18		
temperature	25 °C		
solvent flow	0,4 ml min <sup>-1</sup>		
gradient	acetonitrile / water 65 : 35 (v/v) up to 100 % acetonitrile within 27 min 100 % acetonitrile 5 min		
wave-length (SFM 625)	time (min)	$\lambda$ -exitat. (nm)	$\lambda$ -emiss. (nm)
	0,00	265	350
	11,00	260	380
	14,80	267	430
	18,60	267	435
	22,30	267	460
	26,80	295	460

**Capillary gas chromatography (GC)**

A GC system (GC 5890) of Fa. HEWLETT -PACKARD was used to quantify the chlorinated hydrocarbons. The substances were detected by an Electron Capture Detector (ECD) of HEWLETT- PACKARD. Table 7 shows the chromatographic conditions of the GC.

**Tab. 7: Chromatographic conditions of GC-ECD for CHC**

column	Ultra 1 (HEWLETT- PACKARD) Ø 0,2 mm; length 25 m; film thickness 0,33µm
injector	250 °C
detector	300 °C
temperatures	150 °C 2 min 3 °C min <sup>-1</sup> up to 231 °C 30 °C min <sup>-1</sup> up to 280 °C 280 °C 3 min 5 °C min <sup>-1</sup> up to 300 °C 300 °C 1 min

For a certain identification of substances with an extreme matrix overlay a HEWLETT- PACKARD GC 5890 equiped with a mass selective detector (MS 5972, HEWLETT- PACKARD) was used. Ionization of the sample was due to an electrical pulse ionization. Chromatographic conditions are shown in table 8.

**Tab. 8. Chromatographic conditions for GC-MS**

column	HP 5-MS (HEWLETT-PACKARD) Ø 0,25 mm; length 30 m; film thickness 0,25 µm
injector	270 °C
detector	280 °C
temperatures (CHC)	60 °C 2min 90 °C min <sup>-1</sup> up to 190 °C 6 °C min <sup>-1</sup> up to 250 °C 250 °C 3 min 40 °C min <sup>-1</sup> up to 300 °C 300 °C 3 min
temperatures (PAH)	90 °C 4 min 20 °C min <sup>-1</sup> up to 195 °C 195 °C 2 min 4 °C min <sup>-1</sup> up to 300 °C 300 °C 1 min

### 3.1.3. Hot water extraction

The method of SOM fractionation according turnover rates bases on a chemical hot water extraction. Soils are extracted under reflux on the boiling point of a soil/water (1:5) mixture for one hour. The hot water fraction of SOM is not well defined but contains parts of soil microbial biomass, simple organic compounds and fractions of SOM which can be hydrolysed or depolymerised with water under the given extraction conditions. This is a very easily decomposable fraction of the active SOM (KÖRSCHENS et al. 1990; SCHULZ 1990). The hot water extractable fraction is characterised by its content of carbon and nitrogen. According to the premises of its composition the C/N ratio of this fraction is in the range of the C/N of soil microbial biomass (5...9, <10). A close correlation could be found between the hot water extractable carbon, soil respiration (exhalation of CO<sub>2</sub>) and production of nitrate under

fraction to soil microbial biomass this fraction is of importance for transformation processes of both nutrients and pollutants.

#### 3.1.4. Granulodensimetric fractionation

This is a method of physical fractionation of soil organic matter according to physical properties both into particle size and density fractions. It was developed in Dokuchaev Soil Science Institute (DSSI) and is detailed described by SCHAIMUCHAMETOV & TRAVNIKOVA (1984) and SCHAIMUCHAMETOV et.al. (1984). Fractionation of SOM by this method allows the isolation of soil fractions without any essential changes of their natural properties. This allows to evaluate stability and turnover of soil organic matter on the basis of their interactions with organo minerals.

At first a fraction of plant residues is separated. The specificity of the following method is the separation of the clay fraction ( $< 1\mu\text{m}$  particle size) by treating a soil-water suspension (5:100, w/w) with 15 times ultrasonic energy for each 1 minute.

After this the rest is further divided into 2 soil fractions according to differences in density. The fractionation leads to the following pools:

- „light“ fraction (LF) with a density of  $d < 1,8 \text{ g cm}^{-3}$
- „light“ fraction (LF) with a density of  $1,8 - 2,0 \text{ g cm}^{-3}$
- fractionation rest

The organic matter of the „light“ fraction is characterized by two groups: humic substances such as ripe humic acids and detritus (microbial biomass, biophytolites). These organic substances have no strong bindings to clay minerals. This is the substantial difference in regard to the substances of the „heavy“ fractions. In these „heavy“ fractions the organic substances exist as organo-mineral adsorption complexes (SCHAIMUCHAMETOV et.al. 1984; TRAVNIKOVA et.al. 1990).

Because of the different nature of the organic substances in the „light“ and „heavy“ fractions of soil organic matter they also show different fixation and inactivation properties for nutrients but also pollutants.

### 3.1.5. Pollutants in the granulodensimetric fractions

The determination of organic pollutants in granulodensimetric fractions of soil organic matter could not be done as the determination of total contents (3.1.2.3.). A main problem is the very small mass of the fractions which in most of the cases only was 50 to 150 mg. The extraction method in an overhead shaker or Soxhlett extractor respectively could not be used for this application. A completely **new methodology has been worked out in CER Leipzig-Halle** using a very new extraction technique and equipment from Fa. DIONEX, the Accelerated Solvent Extraction (ASE).

The ASE works on the principle of a solvent extraction but under high pressures and high temperatures. The extraction cells may contain an amount of 10 g soil. They were filled with an inert quartz putting in only a few mg of the contaminated soil or soil fractions (tables 9 and 10).

For the validation of the procedure a large number of comparing investigations were done for testing:

1. comparability of extraction methods used for soil samples of an amount of 10 g
2. comparability of results using different sample sizes down to 100 mg and less.

**Tab. 9: Conditions for the ASE of chlorinated hydrocarbons (CHC)**

solvent	n-hexane/ acetone (1:1, v/v)
heating time	5 min
static extraction time	5 min
flush	60 vol%
purge	60 sec
extraction cycles	1
pressure	100 bar
temperature	100 °C

For the substance class of PAH a comparison was performed for two extraction methods, the cold extraction by shaking in an overhead shaker as described in 3.1.2.3. and the ASE. The results are presented in table 11.

**Tab. 10: Conditions for the ASE of polycyclic aromatic hydrocarbons (PAH)**

solvent	dichloromethane/ acetone (1:1, v/v)
heating time	8 min
static extraction time	8 min
flush	60 vol%
purge	60 sec
extraction cycles	2
pressure	100 bar
temperature	160 °C

**Tab. 11: Comparison of two extraction techniques for PAH from soils**  
(mean of 2 replicates)

PAH	ASE (mg/kg)	cold extraction (mg/kg)	ASE / cold extr. recovery (%)
fluoranthene	82,06	94,40	86,93
pyrene	47,80	75,80	63,06
benzo-c-phenanthrene	4,90	6,90	71,01
benzo-ghi-fluoranthene	5,60	n.d.	
benzo-a-anthracene	20,15	25,00	80,60
chrysene	39,06	32,20	121,30
benzo-e-pyrene	22,42	12,20	183,77
benzo-b-fluoranthene	35,47	41,50	85,47
benzo-k-fluoranthene	18,86	14,10	133,76
benzo-a-pyrene	41,85	23,50	178,09
dibenz-ah-anthracene + benzo-ghi-perylene	21,11	29,00	72,79
coronene	5,48	4,20	130,48
benzo-b-naphtho-2,1-d- thiophene	11,71	n.d.	

Both extraction methods determined the lower condensed PAH in a similar range whereas in some cases the results of the higher condensed PAH using ASE are doubled. This could be due to the extraction conditions of ASE which were set to extract most amounts of PAH possible.

**Tab. 12: Comparison of the content of selected chlorinated hydrocarbons in soil samples in dependence of the sample size**

substance (mg/kg)	sample size				MW (mg/kg)	SD (mg/kg)
	5,0 g	1,0 g	0,5 g	0,1 g		
alpha-HCH	63,93	85,17	88,02	69,52	76,66	9,71
SD (mg/kg)	4,25	0,61	4,75	12,57	4,66	
beta-HCH	465,42	660,02	680,04	579,68	596,29	97,43
SD (mg/kg)	24,73	24,36	54,70	25,79	18,95	
gamma-HCH	1,83	1,66	1,58	1,70	1,69	0,10
SD (mg/kg)	0,08	0,11	0,14	0,43	0,11	
delta-HCH	4,41	5,72	5,41	5,11	5,16	0,56
SD (mg/kg)	0,29	0,40	0,42	0,43	0,15	
HCB	18,25	19,89	18,97	16,24	18,34	1,55
SD (mg/kg)	1,20	0,30	1,13	5,92	1,66	
Aldrine	1,42	0,35	0,26	0,50	0,63	0,53
SD (mg/kg)	0,11	0,03	0,09	0,30	0,09	
Dieldrine	0,12	1,88	1,50	1,41	1,23	0,77
SD (mg/kg)	-	0,23	0,16	0,05	0,19	
p,p'-DDE	0,73	4,14	3,82	3,74	3,11	1,60
SD (mg/kg)	-	0,20	0,18	0,09	0,42	
o,p'-DDD	4,72	8,46	7,40	8,83	7,35	1,86
SD (mg/kg)	0,46	0,63	1,31	4,26	1,39	
p,p'-DDD	8,14	5,13	5,41	12,24	7,73	3,30
SD (mg/kg)	0,55	3,29	5,36	0,40	2,14	

The investigations of the compareability of results for chlorinated hydrocarbons in dependence of the sample size were done with very low amounts of soil down to 100 mg (table 12).

### 3.1.6. Soil microbial biomass

In **Great Britain** the determination of soil microbial biomass carbon was estimated by the method of fumigation-extraction referring JENKINSON & POWLSON (WU et al., 1990) , in **Germany** by the method of substrate induced respiration (SIR) referring ANDERSON & DOMSCH (1978) in an SIR-system of HEINEMEYER et al. (1989).

### 3.1.7. Enzyme activities

The methods used for the determination of various enzyme activities were:

dehydrogenase activity	TTC method referring THALMANN (1968)
$\beta$ -glucosidase activity	modified method in accordance to HOFFMANN & DECKER (1965)
alkaline phosphatase activity	referring TABATABAI & BREMNER (1969)
protease activity	modified method in accordance to LADD & BUTLER (1972)
dimethyl sulph- oxide reduction (DMSO)	referring ALEF & KLEINER; modified by BECK (1991)

## 3.2. RESULTS

For a better understanding and a plausible presentation of the results the contributions of the INTAS project participants are discussed in the following order. This is not an appreciation of the participant's contributions.

**3.2.1. CONTRIBUTION OF GREAT BRITAIN**

**3.2.1.1. Ammonium nitrate extracts**

The elements determined were calcium, cadmium, chromium, copper, iron, potassium, magnesium, manganese, nickel, phosphorus, lead and zinc (Tab. 13). Although, results for iron and phosphorus were obtained, it is very unusual to see results for those elements in this kind of extract. In addition to these, the elements chromium and lead were present in such small quantities that often the concentrations in the extracts were below the detection limit. Therefore, the data for these elements should not be taken as reliable. This also demonstrates the point that chromium and lead are not very soluble and therefore unlikely to be bioavailable in these soils.

**Tab. 13 : Soluble parts of heavy metals in an ammonium nitrate extract**

SAMPLE	HEAVY METAL CONTENT (MG/KG)					
	Ca	Cd	Cr	Cu	Fe	K
<b>BITTERFELD</b>						
SP1	1108,2	0,235	0,513	1,294	13,606	87,487
KEL	1024	0,604	0,108	0,796	0,667	306,1
LAN	1305,4	0,143	0,018	0,082	0,141	179,18
GRE	2412,7	0,125	0,015	0,08	0,026	194,07
<b>LEIPZIG</b>						
37	1802,6	0,074	< 0,000	0,059	0,196	128,69
62,1	1474,5	0,062	0,014	0,099	0,085	99,506
62,2	1709,3	0,061	0,004	0,111	0,045	48,908
63,1	1132,7	0,062	0,009	0,067	0,058	155,21
63,2	2099,5	0,082	0,006	0,385	0,124	98,483
65,1	1070,2	0,059	< 0,000	0,179	0,012	99,067
65,2	1954,7	0,076	0,005	0,257	0,085	80,542
SAMPLE	HEAVY METAL CONTENT (MG/KG)					
	Mn	Ni	P	Pb	Zn	Mg
<b>BITTERFELD</b>						
SP1	7,66	1,33	< 0,000	1,145	16,157	82,107
KEL	6,926	1,359	< 0,000	0,932	39,028	128,83
LAN	4,865	0,2	0,575	0,084	4,169	68,128
GRE	0,696	0,069	0,402	0,016	1,155	158,05
<b>LEIPZIG</b>						
37	1,474	0,023	0,84	0,013	1,207	109,48
62,1	0,812	0,026	0,489	0,055	0,845	80,57
62,2	0,33	0,007	0,443	0,008	0,801	79,488
63,1	1,419	0,02	0,379	0,043	0,805	62,658
63,2	0,217	0,018	0,716	< 0,000	0,83	75,049
65,1	1,716	0,029	< 0,000	< 0,000	1,906	51,554
65,2	0,226	0,066	0,441	0,021	0,765	71,577

### 3.2.1.2. Aqua Regia digests

Because an ICP-AES was used, a large number of channels were switched on when determining the elements on the instrument. This gave results for the concentrations of 19 elements in the soil samples (Tab. 14). The total concentrations of aluminium, barium, calcium, iron, potassium, magnesium, manganese, sodium, strontium and titanium are of relatively little interest, especially as some of these from part of the soil matrix which is not completely destroyed by aqua regia and so are not, strictly speaking, total analyses. However, it is interesting to note that the concentrations of barium appear to be highest in two of the soils which showed to be most polluted in the ammonium nitrate extracts (SPI, KEL). The concentrations of molybdenum in the soils were apparently highest in sample SPI, but the digestion of samples and determination of molybdenum by this technique was shown to be rather unreliable.

Often the remaining potentially toxic metals, taking zinc as an example, it appears that the most polluted soils were KEL, GRE and possibly 63.2 and 65.2. However all of the soils have total zinc concentrations which can be regarded as above background apart from 63.1 and 65.1. It is also of interest that although the total concentrations in SPI were not very high, the soluble amounts (ammonium nitrate extracts) were the second highest of this group of samples. For lead, it appears that soils SPI and KEL were the most contaminated, with LAN not particularly contaminated with this element. The soil KEL was by far the most contaminated with copper and SPI, KEL and GRE most contaminated with chromium. Cadmium appears to follow the zinc contamination, as the greatest total concentrations were in KEL and GRE.

In summary of both sets of results for heavy metals in the soils, it appears that although the soils have above background concentrations, they were not very contaminated with heavy metals, apart from perhaps the zinc contamination in KEL and GRE. The solubility of the zinc appears to be highest in SPI and KEL. It is likely, but dependent on other soil chemical conditions, that the only soil which would be potentially phytotoxic might be KEL.

Tab. 14: Total content of heavy metals in aqua regia digest (Great Britain)

SAMPLE	HEAVY METAL CONTENT (MG/KG DM)						
	Al	Ba	Ca	Cd	Co	Cr	Cu
<b>BITTERFELD</b>							
SPI	12872,43	455,84	2145,2	0,86	8,59	248,07	65,64
KEL	24557,96	843,68	2289,68	3,35	14,31	321,49	139,58
LAN	17160,29	190,66	2957,84	1,39	9,89	38,14	20,13
GRE	20365,55	414,84	8153,1	5,49	14,4	116,51	57,36
<b>LEIPZIG</b>							
37	14553,83	200,07	4482,24	1,27	6,57	19,19	23,86
62,1	11707,67	169,06	3731,36	0,76	4,66	20,76	24,47
62,2	11091,77	211,36	4501,84	1,28	5,57	17,87	38,5
63,1	13546,03	102,28	2573,04	0,34	4,29	17,14	15,06
63,2	11461,51	210,12	6176,72	1,21	5,5	19,66	75,77
65,1	13618,58	101,49	2345,92	0,5	4,29	16,41	18,57
65,2	11105,83	258,74	5961,36	1,22	7,19	19,33	66,93

SAMPLE	HEAVY METAL CONTENT (MG/KG DM)					
	Fe	K	Mg	Mn	Mo	Ni
<b>BITTERFELD</b>						
SPI	34569,53	2772,88	1682,4	193,46	22,44	17,26
KEL	32569,78	2654,4	2815,36	327,42	8,98	31,66
LAN	18923,37	2155,6	2130,4	472,31	2,44	21,63
GRE	29782,97	2237,28	2718,32	890	4,93	39,14
<b>LEIPZIG</b>						
37	15689,61	1927,28	1736,4	448,98	2,14	13,51
62,1	12615,83	1625,76	1403,04	365,52	2,8	32,69
62,2	14456,01	1457,52	1454,56	412,67	0,33	13,4
63,1	10897,13	1941,44	1405,6	297,38	0,82	9,61
63,2	14093,64	1681,68	1505,52	394,22	0,99	13,28
65,1	11030,13	1864,72	1364,64	281,63	0,14	9,64
65,2	15290,76	1561,28	1590	394,38	1,25	14,9

SAMPLE	HEAVY METAL CONTENT (MG/KG DM)					
	Na	P	Pb	Sr	Ti	Zn
<b>BITTERFELD</b>						
SPI	130,22	1905,68	378,54	58,11	1573,28	145,54
KEL	117,14	1626,4	318,22	54,93	1029,2	654,84
LAN	124,75	597,13	67,59	36,48	488,81	220,26
GRE	180,2	1032,72	150,39	81,7	638,5	405,88
<b>LEIPZIG</b>						
37	109,02	802,32	99,15	51,8	433,66	134,07
62,1	93,42	685,43	101,24	42,44	338,44	147,71
62,2	95,78	726,7	146,58	49,15	338,81	209,9
63,1	78,39	564,16	45,43	34,39	409,18	74,82
63,2	87,58	1100,72	165,18	57,27	372,66	270,95
65,1	93,74	556,04	74,43	34,33	418,9	80,14
65,2	121,26	996,08	198,34	58,47	353,15	307,43

**3.2.1.3. Soil biomass carbon**

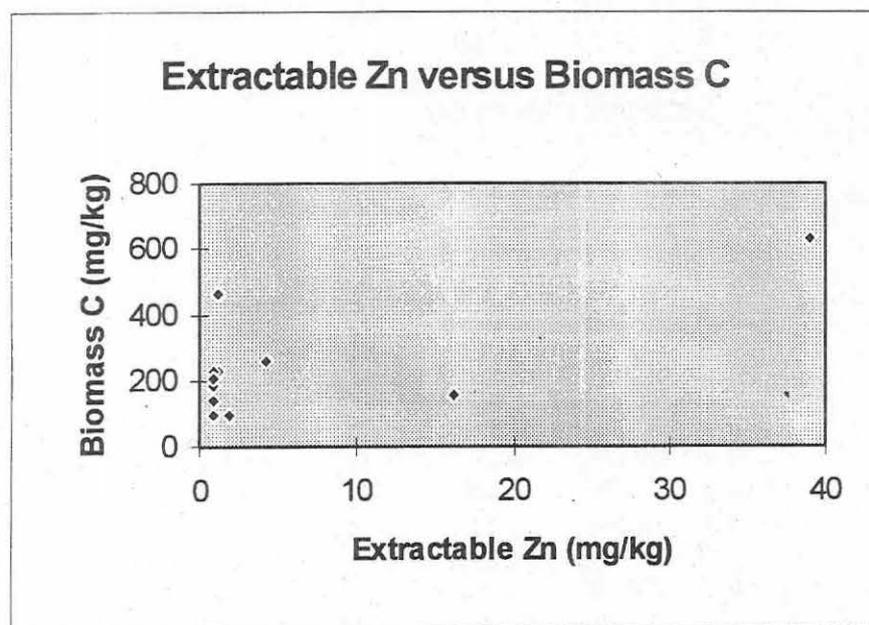
The range of biomass carbon results in these soils was 98 - 633 mg kg<sup>-1</sup>. In accordance to the type of land use occurring at these sites the sample KEL and 37 were of high biomass because they are likely to be a quite productive grassland with high soil organic matter content. The others were mainly in the range 100 - 250 mg kg<sup>-1</sup>, which are characteristic of soils of low carbon status or soils with less productive semi-natural vegetation.

Zinc has been taken as an example, to compare the metal concentration data with the biomass carbon values (Tab. 15).

**Tab. 15: Biomass carbon content in the soils (C<sub>mic</sub> mg kg<sup>-1</sup>)**

Sample	SP1	KEL	LAN	GRE	37	62.1	62.2	63.1	63.2	65.1	65.2
C <sub>mic</sub>	151	634	256	226	464	226	187	98	209	98	141

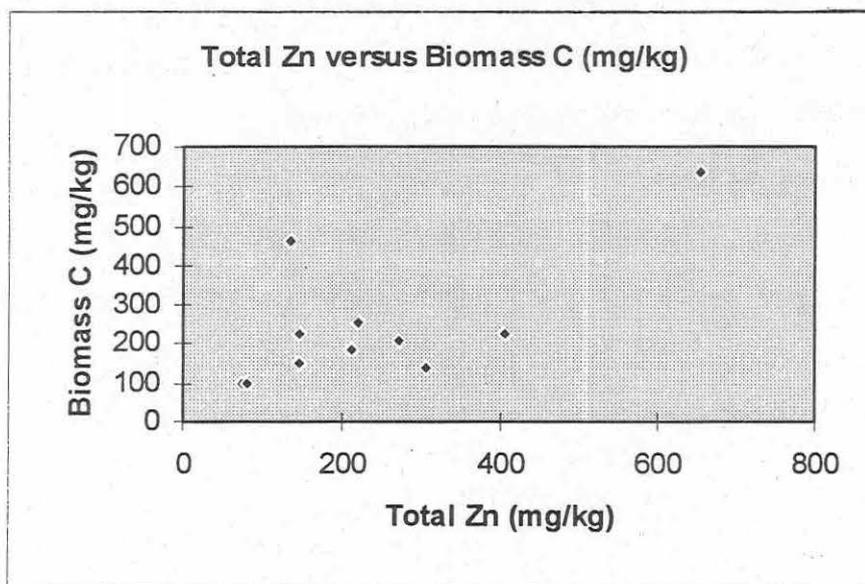
The relationship between ammonium nitrate extractable zinc in the soil and biomass carbon was rather weak (Fig. 1). It is possible that at low concentrations of extractable zinc (> 5 mg kg<sup>-1</sup> extractable), most of the variations in biomass carbon were due to differences in land use and productivity.



**Fig. 1:**  
Relationship between ammonium nitrate extractable zinc and biomass carbon

Of the two sites with high extractable zinc, one (SPI) is of relatively low biomass, and the other (KEL) has both the highest biomass and the highest extractable zinc concentration. This tends to give the impression in Fig. 1 that there was some kind of positive relationship between extractable zinc and biomass, but this is in regard as being by chance, and probably reflects only the nature of the two samples SPI and KEL.

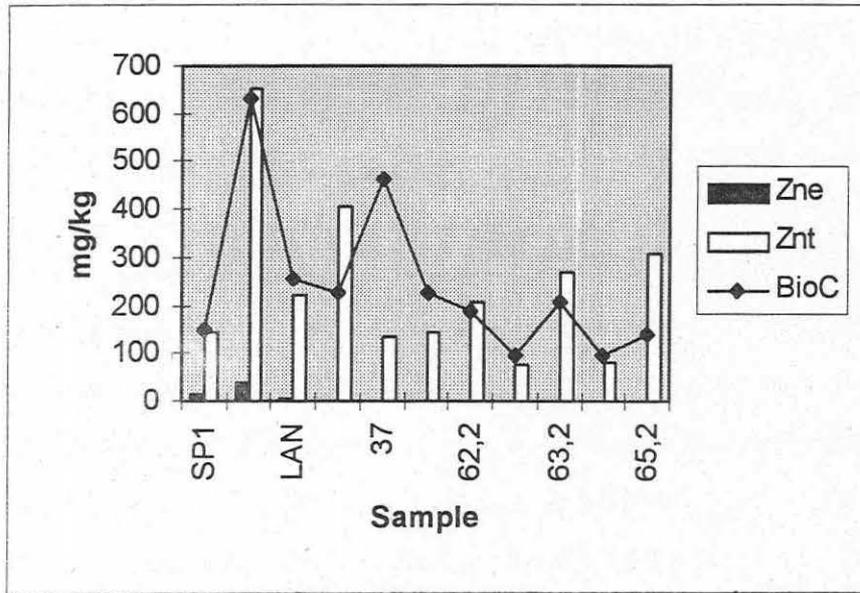
The same general impression is gained when total zinc is plotted against biomass carbon (Fig. 2). However, again this apparent relationship is probably due to other factors relating to the soils. For example, the two soils with the lowest total zinc concentration also happened to have the lowest biomass (63.1 and 65.1). It is likely that these soils are relatively unproductive, therefore leading to low biomass. Soil 37 which has also relatively low total zinc concentration has rather high biomass, probably because of the type of management. Again, the soil with the highest concentration of zinc (KEL) also has the highest biomass. Soil GRE which had the second highest zinc concentration, but a rather low soluble zinc, had a rather intermediate biomass concentration (226mg kg<sup>-1</sup>).



**Fig. 2:**  
Relationship between total content of zinc and biomass carbon

Putting these results together (Fig. 3) shows that the biomass carbon can be high or low in soils with high soluble or total zinc, or in soils with low zinc concentrations. It is likely that similar graphs of other metals such as copper, cadmium, lead would give similar

types of results.



**Fig. 3:**  
**Relationship between both total and extractable zinc and the biomass carbon**

In conclusion it appears that the biomass carbon is not related to the soluble or total concentrations of heavy metals present in these soils. Although most of the samples can be regarded as relatively contaminated, with SPI, KEL, GRE, 63.2 and 65.2 being the most contaminated, it is likely that the toxic thresholds of heavy metals have not been reached in these soils. This could be for a number of reasons, including perhaps most importantly, the pH of these soils and the organic carbon content.

### 3.2.2. CONTRIBUTION OF RUSSIA

#### 3.2.2.1. Total contents of heavy metals in soils

Despite of the fact that the results of determination of heavy metals using RFA or AAS differed, especially for lead and copper, a tendency of similar concentration levels was determined with both analytical methods (table 16).

**Tab. 16: Total contents of selected heavy metals in soils in the wetlands of the river Mulde (mg kg<sup>-1</sup> dm)**

SAMPLE	ANALYTICAL METHOD	SPI	KEL	LAN	GRE	LIMIT VALUE
C <sub>org</sub> (%)		14,7	10,34	1,73	3,1	
Cr	RFA	579	743	106	312	100
Mn	RFA	495	994	692	1278	
Ni	RFA	35	49	25	57	50-100
Cu	RFA	268	242	63	160	55-
	AAS	124	236	24	140	100
Zn	RFA	319	677	310	680	100-300
Pb	RFA	394	423	75	243	32-
	AAS	159	244	35	178	100
Co	AAS	15	10	23	18	50
Cd	AAS	0,7	1,5	0,8	4,1	3-5

According to critical heavy metal limits from BOL'SHAKOV et al. (1993) there were only two soils with increased contents of lead and copper, but all soils were enriched with zinc. Only one sample was enriched in cadmium and nickel respectively.

The contents of Cr, Cu, Zn and Pb were 3- to 13 -fold higher compared to the critical limits.

The total content of the elements zinc, lead, manganese, nickel and cadmium (3- to 8-fold of the critical limit values) is the highest in the heavy wetland soil (GRE).

Sandy-loamy wetland soil SPI was higher contaminated with chromium, copper and lead. These contents were 7- to 13 -fold over the critical limits.

### 3.2.2.2. Heavy metal content of the hot water extractable fraction of soil organic matter

All soils of the wetlands of the river Mulde including the highly contaminated soil KEL showed very low concentrations of heavy metals in the hot water extractable fraction of soil organic matter (table 17). The contents of mobile heavy metals in this fraction were under the limits for drinking water with one exception. The cadmium contents were 2- to 8-fold higher than the critical limits.

**Tab. 17: Hot water extractable contents of heavy metals (AAS) in wetland soils of the river Mulde**

SAMPLE	UNIT	SPI	KEL	LAN	GRE
Cu	mg kg <sup>-1</sup> soil	0,52	0,52	0,21	0,37
	% of the total	0,4	0,2	0,9	0,3
Pb	mg kg <sup>-1</sup> soil	0,023	0,016	0,027	0,038
	% of the total	0,01	0,007	0,08	0,02
Cd	mg kg <sup>-1</sup> soil	0,031	0,041	0,006	0,011
	% of the total	4,4	2,7	0,8	0,3
Co	mg kg <sup>-1</sup> soil	0,165	0,365	0,10	0,010
	% of the total	1,1	3,7	0,04	0,006
Zn	mg kg <sup>-1</sup> soil	7,44	5,90	0,44	0,53

The amounts of copper, lead, cadmium and cobalt in the hot water extract range from 0,01 to 4,4 % of the total contents verifying the low solubility of these elements. The lowest

solubility was found for compounds of lead, but the highest solubility have compounds of cadmium and cobalt (3,5 to 4,4 % of the total).

The wetland soils SPI and KEL having the highest contents of soil organic matter showed the highest content of soluble forms of copper, cadmium, cobalt and zinc. That means large amounts of these elements are bound to organo-mineral complexes. There are tendencies for a positive correlation between soil organic matter and hot water extractable copper, cobalt and zinc but not for the elements lead and cadmium. These results are in accordance to investigations of heavy metals in soil solutions and lysimeter waters (BOLSHAKOV et al. 1993). They found a stimulation of the formation of organo-mineral complexes of heavy metals by dissolved organic compounds. Similar conclusions can be drawn from results of lysimeter investigations of CER Leipzig-Halle, Department Soil Sciences with regard to the influence of dissolved organic carbon on the mobility of heavy metals (KALBITZ 1996).

The hot water extractable copper and lead contents are similar to percolates in lysimeters with the same soils. Heavy metals in the hot water extract of soils seems to provide a reliable method to determine the content of soluble compounds of heavy metals and their disposition for translocation. There was no relationship between total contents of heavy metals and their mobile forms and also no correlation between total soil organic matter, total contents of heavy metals and mobile forms. Sometimes there were even negative correlations. This is due to the complicate and complex processes of the formation of heavy metal compounds of soluble or stable character.

### 3.2.2.3. Distribution of mass parts in the fractions

The mass distribution of the granulodensimetric fractions differ between the soils investigated. The variation of the mass distribution is shown in table 18. The two light textured wetland soils SPI and KEL contain larger amounts of „light“ fractions ( $\Sigma$  LF 21 - 38 %) than the soils LAN and GRE (5 - 10 %). The „light“ fraction (LF) of the soils SPI, KEL and GRE (53 - 74 %) mainly contains the density fraction of  $d < 1,8 \text{ g cm}^{-3}$  whereas the „light“ fraction of soil LAN (65%) mainly contains the density fraction of  $d = 1,8 - 2,0 \text{ g cm}^{-3}$ .

There are only slight differences between the fraction of the physical clay ( $< 1\mu\text{m}$ ) in the 4 soils. The amount of fractionation residue is practically indirect proportional to the accumulation of the „light“ fraction.

**Tab. 18: Mass distribution (%) of the granulodensimetric fractions of the wetland soils of the river Mulde**

Soil	Clay (T) ( $< 1\mu\text{m}$ )	Light fractions (LF)				LF / T	Residual
		Plant residuals	$d < 1,8$ $\text{g cm}^{-3}$	$d=1,8-2,0$ $\text{g cm}^{-3}$	$\Sigma$ LF		
SPI	5,12	2,90	28,08	7,14	38,12	7,4	56,76
KEL	7,10	4,51	10,98	5,22	20,71	2,9	72,19
LAN	5,23	0,61	2,84	6,29	9,74	1,9	85,03
GRE	13,75	0,30	3,24	1,62	5,16	0,4	81,09

#### 3.2.2.4. Distribution of soil organic matter carbon in the granulodensimetric fractions

Because of the very large differences in the total organic carbon of the soils investigated the carbon content of the fractions also vary in a large range (table 19).

For all soils the „light“ fraction of a density of  $d < 1,8 \text{ g cm}^{-3}$  contains the highest percentage of organic carbon (30 - 40 % of the fraction amount) whereas the fraction LF of a density of  $d=1,8 - 2,0 \text{ g cm}^{-3}$  contains a drastic lower amount of organic carbon (6 - 20 %).

The carbon content of the clay fraction varies between 6 - 18 %.

**Tab. 19: Distribution of the carbon content in the granulodensimetric fractions of the wetland soils of the river Mulde**

soil	total soil $C_{org}$ (%)	clay fract. $C_{clay}$	ligh fraction - $C_{LF}$ (%)			residual $C_R$	
			$d < 1,8$ $g\ cm^{-3}$	$d = 1,8-2,0$ $g\ cm^{-3}$	$\Sigma LF$		
SPI	a*)	17,70	39,77	21,14		1,52	
	b*)	14,70	0,91	11,17	1,51	12,68	0,86
	c*)		6,2	76,0	10,3	86,3	5,9
KEL	a*)	12,92	30,78	20,36		1,72	
	b*)	10,34	0,92	3,38	1,06	4,44	1,24
	c*)		8,9	32,5	10,3	42,8	12,0
LAN	a*)	10,23	28,63	5,74		0,46	
	b*)	1,73	0,54	0,81	0,36	1,17	0,39
	c*)		31,2	46,8	20,8	67,6	22,6
GRE	a*)	6,15	31,20	14,36		1,22	
	b*)	3,10	0,84	1,01	0,23	1,24	1,04
	c*)		27,3	32,6	7,5	40,1	33,5

a\*) in % of the amount of the fraction

b\*) in % soil mass

c\*) carbon content in % of the total

Comparing the high carbon content of the „light“ fraction in the wetland soils (40 - 86 % of the total carbon content) with data from selected agricultural used soils of Russia and Germany (TRAVNIKOVA et al. 1992) there are some features. There are the large differences in the total carbon content and the amount and carbon content of the „light“ and clay fraction respectively. Possibly this is due to different soil forming conditions. Remarkable on the other hand is the comparatively high total carbon content of the soils SPI and KEL and their carbon content in „light“ fractions. As an example, in a very fertile agricultural used Tschernozem the amount of carbon in the „light“ fraction (in % of fraction mass) ranges from 0,5 to 1,8 % which is not more than 30 - 50 % of the total

carbon content of the soil. In the wetland soil SPI the amount of carbon in the „light“ fraction is at about 13 % of the fraction mass which represents 86 % of the total carbon content of the soil.

These features of the humus state of the wetland soils are of particular importance for the determination of the stability of the dominant forms of heavy metal compounds and their transformation behaviour.

### 3.2.2.5. Distribution of inorganic pollutants in the granulodensimetric fractions

As already indicated the wetland soils only have increased contents of lead and copper. A contamination with cadmium was only detected in soil GRE.

The concentrations of metals (mg/kg of the fraction) vary widely.

Irrespective of the absolute contamination degree higher amounts of cobalt, cadmium and lead were found in the clay fraction and higher amounts of copper were found in the „light“ fraction with  $d < 1,8 \text{ g cm}^{-3}$  (exception: sandy wetland soil where a maximum content of copper and cobalt was found in the fractionation residue).

The concentrations of heavy metals in the two density fractions of the „light“ fraction follow the same order. This „light“ fraction contains also biophytolites with active adsorption centres of silicium groups (SCHAIMUCHAMETOV et al. 1984; BARTOLLI 1985). The Si-group specific adsorption of heavy metals occurs analogue to the adsorption type of aluminium but with less stability (BOL'SHAKOV et al. 1993).

Investigations to forms of heavy metal bindings and mechanisms of their transformation have to be done. However, one hypothesis is that lead, cobalt and cadmium is strongly linked to adsorption processes on the surface of clay particles while copper is unlinked to humic substances of the „light“ fraction with  $d < 1,8 \text{ g cm}^{-3}$ .

Tab. 20: Distribution of heavy metals in the granulodensimetric fractions of wetland soils of the river Mulde

soil	fractions	copper			cobalt			cadmium			lead		
		a*)	b*)	c*)	a*)	b*)	c*)	a*)	b*)	c*)	a*)	b*)	c*)
SPI	plant residuals	106,3	3,1		6,67	0,2		1,04	0,03		250,0	0,03	
	LF, $d < 1,8 \text{ g cm}^{-3}$	58,75	16,5		4,44	1,2		1,2	0,30		119,3	335	
	LF, $d = 1,8-2,0 \text{ g cm}^{-3}$	43,75	3,1		4,40	0,3		0,24	0,02		431,8	30,8	
	$\Sigma$ LF	-	22,7	18	-	1,7	10	-	0,35	50	-	64,33	45
	clay ( $< 1\mu\text{m}$ )	125,0	6,4	5	13,2	0,7	5	0,96	0,05	7	1150,0	79,0	50
	fract. residue	169	96	77	23	13	87	0,5	0,3	43	16	9	6
	total content	-	125	-	-	15	-	-	0,7	-	-	159	-
KEL	plant residuals	87,5	3,9		6,67	0,3		2,0	0,09		272,7	12,3	
	LF, $d < 1,8 \text{ g cm}^{-3}$	283,8	31,2		4,40	0,5		1,60	0,2		400,0	43,9	
	LF, $d = 1,8-2,0 \text{ g cm}^{-3}$	175,0	9,1		8,88	0,5		1,68	0,09		448,9	23,4	
	$\Sigma$ LF	-	44,2	19	-	1,3	13	-	0,38	25	-	79,6	32
	clay ( $< 1\mu\text{m}$ )	143,8	102	4	20,0	1,4	14	3,4	0,2	13	1250,0	88,8	36
	fract. residue	253	183	77	10	7	70	1,0	0,9	60	105	76	31
	total content	-	237	-	-	10	-	-	1,5	-	-	245	-
LAN	plant residuals	25,0	0,2		11,1	0,07		2,92	0,02		79,5	0,5	
	LF, $d < 1,8 \text{ g cm}^{-3}$	118,8	3,4		6,67	0,2		1,08	0,03		267,0	7,6	
	LF, $d = 1,8-2,0 \text{ g cm}^{-3}$	10,0	0,6		6,60	0,4		0,56	0,04		113,6	7,1	
	$\Sigma$ LF	-	4,2	18	-	0,67	3	-	0,09	11	-	15,2	43
	clay ( $< 1\mu\text{m}$ )	81,3	4,3	18	31,1	1,6	7	4,0	0,2	25	348,9	18,2	10
	fract. residue	21	15,5	63	25	21	91	0,6	0,5	63	2	2	6
	total content	-	24	-	-	23	-	-	0,8	-	-	35	-
GRE	plant residuals	105,6	0,3		9,26	0,03		5,22	0,02		118,3	0,35	
	LF, $d < 1,8 \text{ g cm}^{-3}$	425,0	13,8		17,8	0,6		6,48	0,2		511,4	16,6	
	LF, $d = 1,8-2,0 \text{ g cm}^{-3}$	125,0	2,0		17,8	0,3		3,28	0,05		323,9	5,2	
	$\Sigma$ LF	-	16,1	12	-	0,93	5	-	0,27	7	-	22,1	12
	clay ( $< 1\mu\text{m}$ )	118,8	16,3	12	46,7	6,40	36	9,4	1,30	32	517,0	71,1	40
	fract. residue	133	108	77	14	11	61	3	2,5	61	106	86	50
	total content	-	140	-	-	18	-	-	4,1	-	-	179	-

a\*)  $\text{mg kg}^{-1}$  of the fraction  
 b\*)  $\text{mg kg}^{-1}$  of the soil  
 c\*) % of the total content

This is because of:

- the high affinity of these elements to humic substances especially to the group of humic acids (ORLOV 1985; BOL'SHAKOV et al. 1993) and
- the active role of copper in the transformation processes of soil organic matter (MORTLAND 1970).

The coarse fraction of the soils contains the main parts of chromium, manganese, cadmium and cobalt (Tab. 21) whereas zinc and lead were mainly found in the two „light“ fractions and in the clay fraction.

**Tab. 21: Content of heavy metals in the coarse fraction of wetland soils of the river Mulde**

soil	Cr		Cu		Zn		Pb		Ni	
	a*)	b*)								
<b>SPI</b>	455	79	19	7	47	15	32	8	10	29
<b>KEL</b>	334	45	53	22	240	35	56	13	16	33
<b>LAN</b>	55	52	8	13	35	11	15	20	6	10
<b>GRE</b>	201	64	56	35	318	47	44	19	36	63

a\*) mg kg<sup>-1</sup> of soil

b\*) % of the total content

There are tendencies for a correlation between Cu, Zn, Ni, Pb, Cr and the carbon content of the residual fraction. This may be because of the dominate organic nature of the metal compounds in the fractionation residual.

Table 22 shows which fraction of the soil is enriched with heavy metals. Enrichment coefficients were calculated for the elements copper, cobalt, cadmium and lead in the wetland soils SPI, KEL and GRE with the low contaminated soil LAN as basis line.

**Tab. 22: Coefficients for an enrichment of selected heavy metals in different soil fractions of wetland soils compared with an only little contaminated soil**

soil	soil fractions	Cu	Co	Cd	Pb
SPI	plant residuals	4	-	-	3
	LF, $d < 1,8 \text{ g cm}^{-3}$	-	-	-	-
	LF, $d = 1,8 - 2,0 \text{ g cm}^{-3}$	4	-	-	4
	clay ( $< 1 \mu\text{m}$ )	1,5	-	-	4,5
	fractionation residual	8	-	-	8
KEL	plant residuals	3,5	-	-	3,5
	LF, $d < 1,8 \text{ g cm}^{-3}$	2,5	-	-	1,5
	LF, $d = 1,8 - 2,0 \text{ g cm}^{-3}$	17,5	-	3	4
	clay ( $< 1 \mu\text{m}$ )	2	-	-	4
	fractionation residual	12	-	1,5	53
GRE	plant residuals	4	-	2	1,5
	LF, $d < 1,8 \text{ g cm}^{-3}$	4	2,5	6	2
	LF, $d = 1,8 - 2,0 \text{ g cm}^{-3}$	12,5	3	6	3
	clay ( $< 1 \mu\text{m}$ )	1,5	1,5	2	1,5
	fractionation residual	6	-	5	53

From the results of table 22 it can be concluded that increasing contamination degrees results in enrichments of heavy metals in all organo-mineral soil fractions as well as in the fractionation residue. The rates of enrichments are different for elements and fractions. Increasing contamination degrees cause an accumulation of copper and lead mostly in the „light“ fraction of  $d = 1,8 - 2,0 \text{ g cm}^{-3}$  and in the clay fraction. This is in accordance to the conclusion of adsorption processes of heavy metals by biophytolites.

### 3.2.3. CONTRIBUTION OF GERMANY

#### 3.2.3.1. Total contents of organic pollutants in wetland soils of the river Mulde

In some wetland soils of the river Mulde not only a contamination with heavy metals but also with organic pollutants was detected. Main organic pollutant in this region is the  $\beta$ -isomer of the hexachlorocyclohexane ( $\beta$ -HCH), a waste-product of the lindane ( $\gamma$ -hexachlorocyclohexane) production process. Lindane was formerly used as a pesticide agent. Because of the high persistence of the  $\beta$ -HCH in all environmental compartments investigations are necessary for an evaluation of its long term behaviour.

**Tab. 23: Total content of selected chlorinated hydrocarbons ( $\text{mg kg}^{-1}$ ) in wetland soils of the river Mulde**

	SPI	KEL	LAN	GRE	G1	G2	G3
alpha-HCH	77,527	44,797	0,033	0,818	0,996	1,333	0,361
HCB	19,081	14,318	0,008	0,521	0,740	0,956	0,097
beta-HCH	<b>152,651</b>	<b>239,271</b>	<b>0,120</b>	<b>15,272</b>	<b>1,568</b>	<b>15,430</b>	<b>2,511</b>
gamma-HCH	2,437	0,716	0,018	0,052	0,054	0,021	n.d.
delta-HCH	3,851	2,141	0,015	0,095	0,564	0,236	0,032
aldrine	0,351	0,071	0,007	0,083	-	-	-
DDT-group	16,275	17,549	n.d.	3,063	-	-	-
methoxychlor	18,713	4,349	n.d.	n.d.	-	-	-

n.d. = not detected

Total concentrations of the organo-chemicals in soils show the high contamination degree (Tab. 23) but also the large variation between the sites. As already mentioned in previous chapters, the soil LAN is only little contaminated with both heavy metals and organic pollutants.

The other soils of Germany, Russia and North Bohemia were not contaminated with chlorinated hydrocarbons what is in accordance to their genesis and use.

Tab. 24: Total content of selected polycyclic aromatic hydrocarbons in urban soils and ash substrates (mg kg<sup>-1</sup>)

soil	fluor-anthene	pyrene	benzo(a)-anthracene	benzo(b)-fluoranthene	benzo(k)-fluoranthene	benzo(a)-pyrene	Σ of 10 PAH
<b>Leipzig</b>							
37	0,66	0,36	0,35	0,43	-	-	1,79
62.1	0,45	0,26	0,31	0,44	0,16	0,19	2,06
62.2	0,79	0,35	0,35	0,67	0,26	0,35	6,90
63.1	0,31	0,13	0,14	0,16	0,07	0,09	1,24
63.2	1,52	0,87	1,01	1,40	0,53	0,91	7,88
65.1	0,42	0,27	0,17	0,21	0,09	0,08	1,61
65.2	5,05	3,44	2,21	3,02	1,17	2,01	22,26
<b>Moscow</b>							
<b>city</b>							
1	0,20	0,13	0,15	0,17	0,05	0,08	1,01
2	0,03	<0,05	<0,025	<0,025	<0,013	<0,025	0,22
3	0,15	0,16	0,25	0,04	<0,013	<0,025	0,77
4	0,43	0,15	0,11	0,19	0,05	0,05	1,38
5	0,16	<0,1	0,06	0,09	0,03	0,06	0,72
6	0,10	<0,1	0,05	0,05	0,02	<0,025	0,55
7	0,08	<0,1	0,05	0,03	<0,013	<0,025	0,49
8	0,13	0,05	0,05	0,07	0,03	0,05	0,61
<b>steel mill</b>							
1	0,15	0,05	0,013	0,025	<0,006	<0,013	0,37
2	0,20	0,09	<0,013	0,020	<0,006	<0,013	0,42
3	-	0,09	0,04	0,071	0,019	0,023	0,42
4	0,14	<0,05	0,02	0,037	0,009	<0,013	0,38
5	0,15	<0,05	0,02	0,037	-	<0,013	0,38

It was assumed that in the urban soils of Russia and Germany and in the ash substrates of North Bohemia larger amounts of PAH would be found. Table 24 shows that these soils contain only very small amounts of PAH with the exception of the second layer of the urban soil (65.2) of Leipzig (Stephanieplatz). This could be due to the fact that city sites sometimes get new soil material as an overlay on the former top soil layer.

### 3.2.3.2. Organic pollutants in a hot water extractable fraction of soil organic matter

There are only few informations about the behaviour of  $\beta$ -HCH in soil but it seems to be a problematic substance because of its hydrophobic properties and the high persistence in soil. Until now there are some views that because of its hydrophobic properties there are minimum risks for a translocation of  $\beta$ -HCH in deeper soil layers and the ground water as well as minimum risks to get into the food chain.

Investigations in the CER, Department Soil Sciences showed that  $\beta$ -HCH could be found also in deeper soil layers (KALBITZ 1996) and that  $\beta$ -HCH was taken up from contaminated soils in significant amounts by carrots, broad beans and maize (HEINRICH & SCHULZ 1996 a,b,c,d.).

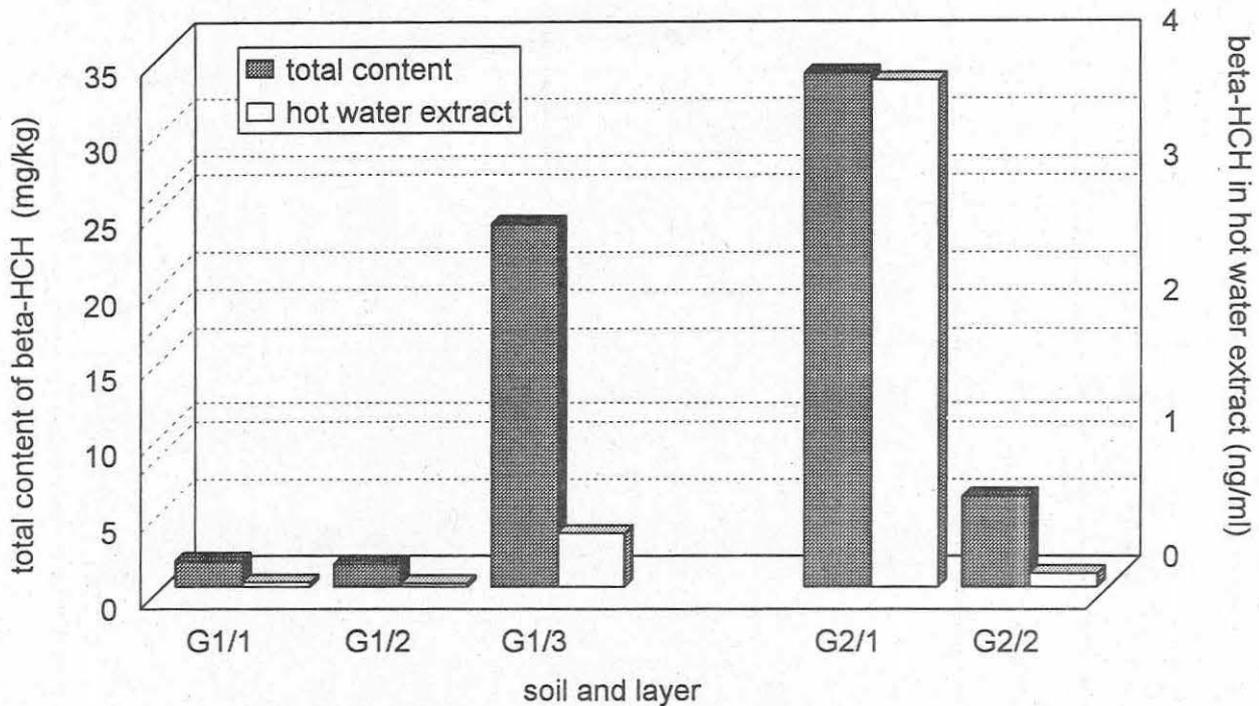
Further on in the past years some agricultural land in the riverine areas of the river Mulde had to be excluded from being used as pasture or for feed-stuff production as a consequence of the appearance of  $\beta$ -HCH in cow milk.

Analyzing some other sites of the wetlands of the river Mulde for their total contents but also soluble and available amounts especially of  $\beta$ -HCH the following could be concluded (SCHULZ & KLIMANEK 1996):

The two sites (G1 and G2) were investigated also in deeper soil layers. The highest contamination with  $\beta$ -HCH was found in the third layer of soil G1 while in soil G2 the first layer was most contaminated (Fig. 4).

No or insignificant amounts of this substance were found in the soil solution. However, in the hot water extractable fraction of soil organic matter the  $\beta$ -HCH amounted between 8 to 11 % of the total content (Fig. 4).

**Fig. 4:** Content of  $\beta$ -HCH as a total and in hot water extract respectively in wetland soils of the river Mulde (SCHULZ & KLIMANEK 1996)



The fraction of hot water extractable soil organic matter contains microbial biomass but also slightly decomposable organic matter. This fraction is strongly correlated to soil biological processes and parameters (SCHULZ 1990) and may be used for an evaluation of the soil nutrient supply as well as the bio-availability of pollutants (TITOVA et al. 1995).

**3.2.3.3. Organic pollutants in granulodensimetric fractions of wetland soils of the river Mulde**

This novel analytical method has been used to evaluate if organo-chemicals can be detected in very low concentrations and in very small samples. First results for selected compounds of the group of chlorinated hydrocarbons in the wetland soils SPI, KEL, LAN and GRE are presented.

Tab. 25: Distribution of selected chlorinated hydrocarbons (CHC) in wetland soils SPI and KEL of the river Mulde

soil	contents of CHC in granulodensimetric fractions										Σ fractions
	clay (< 1µm)		plant residuals		LF <1,8 g cm <sup>-3</sup>		LF=1,8-2,0 g cm <sup>-3</sup>		residue		
	mg kg <sup>-1</sup>	mg/fract	mg kg <sup>-1</sup>	mg/fract	mg kg <sup>-1</sup>	mg/fract	mg kg <sup>-1</sup>	mg/fract	mg kg <sup>-1</sup>	mg/fract	mg
<b>SPI</b>											
alpha -HCH	11,83	0,61	22,15	0,64	22,89	6,43	16,40	1,17	0,11	0,06	8,91
HCB	6,82	0,35	11,82	0,34	7,02	1,97	5,54	0,40	0,03	0,02	3,07
<b>beta-HCH</b>	<b>110,74</b>	<b>5,67</b>	<b>95,99</b>	<b>2,78</b>	<b>18,64</b>	<b>5,23</b>	<b>13,84</b>	<b>0,99</b>	<b>0,25</b>	<b>0,14</b>	<b>14,82</b>
gamma-HCH	2,02	0,10	2,09	0,06	2,93	0,82	2,66	0,19	0,16	0,09	1,27
delta-HCH	2,07	0,11	2,73	0,08	1,18	0,33	1,38	0,10	0,01	0,01	0,62
aldrine	0,23	0,01	0,15	0,004	0,36	0,10	0,17	0,01	0,07	0,04	0,17
Σ DDT-group		0,86		0,50		0,78		0,29		0	2,54
o,p' methoxychlor	4,08	0,21	7,44	0,22	0,87	0,24	1,31	0,09	0	0	0,76
p,p' methoxychlor	17,37	0,89	28,34	0,82	4,20	1,18	3,14	0,22	0,22	0,13	3,24
<b>KEL</b>											
alpha -HCH	6,16	0,44	15,24	0,69	37,70	4,14	58,98	3,08	0,42	0,31	8,65
HCB	2,28	0,16	6,59	0,30	5,80	0,64	18,09	0,94	0,17	0,12	2,16
<b>beta-HCH</b>	<b>120,47</b>	<b>8,55</b>	<b>275,03</b>	<b>12,40</b>	<b>48,47</b>	<b>5,32</b>	<b>68,92</b>	<b>3,60</b>	<b>0,88</b>	<b>0,63</b>	<b>30,51</b>
gamma-HCH	0,81	0,06	1,24	0,06	4,39	0,48	4,65	0,24	0,32	0,23	1,07
delta-HCH	0,93	0,07	1,88	0,09	0,97	0,11	1,32	0,07	0,04	0,03	0,35
aldrine	0,10	0,01	0,69	0,03	0,18	0,02	0,25	0,01	0,04	0,03	0,10
Σ DDT-group		0,74		0,75		0,66		0,49		0,10	2,73
o,p' methoxychlor	0,75	0,05	0	0	0,86	0,09	1,25	0,07	0,08	0,06	0,27
p,p' methoxychlor	1,78	0,13	2,18	0,10	2,72	0,30	3,56	0,19	0,38	0,28	0,99

Tab. 26: Distribution of selected chlorinated hydrocarbons (CHC) in wetland soils LAN and GRE of the river Mulde

soil	contents of CHC in granulodensimetric fractions										Σ fractions
	clay (< 1µm)		plant residuals		LF <1,8 g cm <sup>-3</sup>		LF=1,8-2,0 g cm <sup>-3</sup>		residue		
	mg kg <sup>-1</sup>	mg/fract	mg kg <sup>-1</sup>	mg/fract	mg kg <sup>-1</sup>	mg/fract	mg kg <sup>-1</sup>	mg/fract	mg kg <sup>-1</sup>	mg/fract	mg
<b>LAN</b>											
alpha -HCH	0,51	0,03	0,41	0,002	0,49	0,01	0,50	0,03	0,01	0,01	0,03
HCB	0,15	0,01	0	0	0	0	0,16	0,01	0	0	0,01
beta-HCH	<b>7,04</b>	<b>0,37</b>	<b>8,59</b>	<b>0,05</b>	<b>3,03</b>	<b>0,09</b>	<b>1,00</b>	<b>0,06</b>	<b>0,06</b>	<b>0,05</b>	<b>0,12</b>
gamma-HCH	0,49	0,03	0,28	0,002	0,75	0,002	0,43	0,03	0,04	0,03	0,02
delta-HCH	0,07	0,004	0	0	0,10	0,003	0,05	0,003	0,01	0,01	0,02
aldrine	0,03	0,002	0,02	0	0,31	0,01	0,10	0,01	0,02	0,01	0,01
Σ DDT-group		0,002		0		0		0		0	0
o,p' methoxychlor	0	0	0	0	0	0	0	0	0	0	0
p,p' methoxychlor	0	0	0	0	0	0	0	0	0	0	0
<b>GRE</b>											
alpha -HCH	0,28	0,04	n.s.	n.s.	0,73	0,02	1,23	0,02	0,06	0,05	0,13
HCB	0,07	0,01	n.s.	n.s.	0,34	0,01	0,49	0,01	0	0	0,3
beta-HCH	<b>5,18</b>	<b>0,71</b>	n.s.	n.s.	<b>6,55</b>	<b>0,21</b>	<b>8,11</b>	<b>0,13</b>	<b>0,35</b>	<b>0,28</b>	<b>1,34</b>
gamma-HCH	0,35	0,05	n.s.	n.s.	1,27	0,04	1,51	0,02	0,20	0,16	0,27
delta-HCH	0,06	0,01	n.s.	n.s.	0	0	0	0	0	0	0,01
aldrine	0,01	0,001	n.s.	n.s.	0	0	0,18	0,003	0,01	0,01	0,01
Σ DDT-group		0,24		n.s.		0		0		0	0,24
o,p' methoxychlor	0	0	n.s.	n.s.	0	0	0	0	0	0	0
p,p' methoxychlor	0	0	n.s.	n.s.	0	0	0	0	0	0	0

The project co-operators of Russia did the granulodensimetric fractionation of the wetland soils SPI, KEL, LAN and GRE. The mass of the fractions the organics were analyzed from ranged only between some 50 mg to some 200 mg where (Tab. 25, 26). The results are comparable to the original method with larger samples. The main contaminant is the  $\beta$ -isomer of hexachlorocyclohexane ( $\beta$ -HCH). The content of  $\beta$ -HCH varies widely between sites following the order: KEL > SPI > GRE > LAN. The sites KEL and SPI show also the highest concentrations and amounts of the other analysed chlorinated hydrocarbons (CHC) but the distribution in the fractions differs. In all cases no considerable concentrations of CHC were found in the fractionation residue while highest concentrations and amounts of  $\beta$ -HCH were found in the clay fraction (<1 $\mu$ m) and in the plant residuals. The high concentrations in the clay fraction reveals the possible importance of adsorption processes in the fate of  $\beta$ -HCH which also form complexes with soil organic matter. Whithin the „light“ fractions accumulation of  $\beta$ -HCH was found in all density fractions. In the much less polluted sites GRE and LAN the  $\beta$ -HCH is found in same amounts in all fractions except the fractionation residue. Highest concentrations of methoxychlor accumulated in the clay fractions and plant residuals have been found in soils of the site SPI where the original soil contains relatively large amounts. In soils of the site KEL methoxychlor concentrations were much lower and the distribution of this substance is nearly equal in the fractions (except the residues).

The high concentrations of the  $\beta$ -HCH in the fraction of plant residuals is due to uptake by living plants (especially roots) which accumulate considerable amounts (HEINRICH & SCHULZ 1996).

### 3.2.3.4. Parameters of soil biological activity

Anthropogeneous activities on the soil may influence the biological activity of soil micro-organisms.

Using three wetland soils of the river Mulde and two soils of the city of Leipzig the influence of heavy metals and organic pollutants on selected criteria of biological activity of soil micro-organisms was tested. For an evaluation of the soil microbial activity a number of parameters are necessary because the impact between harmful substances may cause different effects on soil micro-organisms.

The results of the biological investigations are presented in table 27 and 28.

Investigated soils differed in their contamination degree for heavy metals and organic pollutants. Site KEL was the most polluted one. The content of heavy metals and polycyclic aromatic hydrocarbons (PAH) were mostly in the range of the category B of the „Holland List“. In the wetland soil SPI the content of chromium was found to be even above category B while its contents of cadmium, copper, zinc and PAH were within category B, above the critical limits of the category A of the „Holland List“.

#### **Soil microbial biomass**

Microbial biomass (Tab. 27) did not correlate with the degree of pollution. The lowest amount of microbial biomass carbon was found in the soil SPI. The microbial biomass was twice as high in the most polluted soil KEL. The only slightly contaminated soil LAN had the highest microbial biomass

Similar results were found with the urban soils of Leipzig (Tab. 28). At site Stephanieplatz soils of two layers had been sampled at different places. The samples varied in the amount of microbial biomass and the degree of contamination also ranged in the categories A and B for the elements lead, copper, zinc and barium. Higher contamination degree was found in the deeper soil layer. A drastic decrease of soil microbial biomass with increasing heavy metal contamination as reported by KANDELER (1990), CHANDER (1990) and FILIP (1995) was not found. However, in these investigations the contamination degree was much below the limitation values reported by KLOKE (1980).

Tab. 27: Parameters of biological activity of wetland sites of the river Mulde

	SPI	KEL	LAN
soil layer (cm)	0-20	0-20	0-20
TOC (%)	16,96	12,90	2,93
$\Sigma$ CO <sub>2</sub> g <sup>-1</sup> soil after 120 days incubation	2,20	0,80	1,60
production rate $\mu\text{g CO}_2 \text{ g}^{-1} \text{ d}^{-1}$			
start	30,70	17,30	30,40
end	16,20	5,00	1,00
hot water extractable C (mg g <sup>-1</sup> )	2,1	1,2	2,2
biomass C <sub>mic</sub> ( $\mu\text{g g}^{-1} \text{ dm}$ )	108,53	217,99	374,5
basic respiration ( $\mu\text{gCO}_2\text{-C g}^{-1} \text{ h}^{-1}$ )	1,54	2,87	3,44
metabolic quotient qCO <sub>2</sub> ( $\text{ng C} \mu\text{g}^{-1} \text{C}_{\text{mic}}$ )	14,19	13,14	9,17
dehydrogenase ( $\mu\text{g TPF g}^{-1} \text{ dm}$ )	0	5,37	11,34
DMSO reductase ( $\text{ng DMSO g}^{-1} \text{ h}^{-1}$ )	214	642	1554
nitrification N <sub>inorg.</sub> ( $\mu\text{g g}^{-1}$ )			
start	4,5	4,1	4,7
end	141	55,8	114,1

In long term incubation experiments a negative effect of increasing contamination with pollutants on the metabolic activity was found in the soil KEL (Tab. 27). Despite of a high amount of organic carbon and a relatively high content of easy mineralizable carbon (carbon of the hot water extractable fraction of soil organic matter - C<sub>hwe</sub>) only 0,8 mg C per g soil were mineralized in the soil KEL during an incubation time of 120 days. In contrast to this in the soil SPI 2,2 and in the soil LAN 1,6 mg C per g soil were mineralized.

In the soil KEL only 56 % of the hot water extractable carbon were mineralized while in the soil SPI more than the amount of this carbon fraction was mineralized (see  $\Sigma$  of CO<sub>2</sub> production and hot water extractable carbon in Table 27).

The soil SPI showing a contamination of heavy metals within the range of the A category of the „Holland List“ and having the highest content of organic carbon showed the highest CO<sub>2</sub> production rate in the end of the long term incubation.

Tab. 28: Parameters of biological activity of urban sites of Leipzig

	Mariannen-	Stephanieplatz					
	park MAR 2	62.1	62.2	63.1	63.2	65.1	65.2
horizon	Ah	Ah	Ah	Ah	Ah	Ah	Ah
depth (cm)	11	8	20	17	9	22	18
TOC (%)	3,97	1,8	2,41	1,48	3,35	1,28	2,94
incub. (mg CO <sub>2</sub> 100g <sup>-1</sup> ) after 35 days	202,51	141,95	93,96	107,04	111,87	99,88	105,6
biomass C <sub>mic</sub> (µg g <sup>-1</sup> dm)	528,75	415,84	255,77	292,89	240,3	230,78	183,65
basic respiration (µgCO <sub>2</sub> -C g <sup>-1</sup> h <sup>-1</sup> )	3,37	2,64	1,84	2,08	2,13	1,54	1,82
metabolic quotient qCO <sub>2</sub> (ng Cµg <sup>-1</sup> C <sub>mic</sub> )	6,37	6,34	7,19	7,11	8,86	6,6	9,91
dehydrogenase (µg TPF g <sup>-1</sup> dm)	65,84	68,01	27,43	46,07	28,28	30,69	12,14
alc. phosphatase (mg p-nitrophenole g <sup>-1</sup> )	2476	2408	2334	953	2588	527	2474
protease (µg tyrosine g <sup>-1</sup> 2h <sup>-1</sup> )	868	359	381	220	387	156	283
β-glucosidase (µg argenine g <sup>-1</sup> 3h <sup>-1</sup> )	219,33	121,59	111,56	82,35	102,87	71,66	83,66
DMSO reductase (ng DMSO g <sup>-1</sup> h <sup>-1</sup> )	2877	1369	790	992	759	941	477

As an indirect and more practicable criterion for the microbial transformation efficiency in dependence of the contamination degree of soils the metabolic quotient for CO<sub>2</sub> (q CO<sub>2</sub>) can be used (ANDERSON & DOMSCH 1989). The metabolic quotient (q CO<sub>2</sub>) of the heavy polluted soil SPI and KEL is increased drastically. Similar results were found by INSAM(1990) and KANDELER (1990).

In unpolluted soils values between 2 and 8 ng CO<sub>2</sub>-C per µg C of microbial biomass and hour are measured depending on the kind of land use of the soils and the determination method respectively (BECK 1991) . The metabolic quotient of the soils investigated was about 14 indicating that in these soils contaminated with heavy metals and PAH the energy demand of micro-organisms for their maintenance respiration was higher, e.g. more substrate was transformed to CO<sub>2</sub> and therefore less energy was converted into soil microbial biomass.

The metabolic quotients of the urban soils of Leipzig ranged in the same order although the stress situation for micro-organisms was classified below the critical limit.

### **Nitrification efficiency**

At the beginning and at the end of an incubation experiment the wetland soils of the river Mulde had similar amounts of mineral nitrogen (N<sub>inorg</sub>) but there were big differences in nitrification efficiency at the end of the incubation. No correlation to the C/N ratio or the content of organic carbon could be found.

The nitrification efficiency was high at the slightly contaminated sites SPI and LAN compared to the more contaminated site KEL with its much higher content of organic carbon and nitrogen. However, the nitrification efficiency of site KEL was 40 to 50 % of that of the two other sites. The reduction in nitrification is possibly due to the enrichment of especially cadmium and lead which may be over a tolerance threshold (KANDELER et al. 1990 and 1992; TYLER et al. 1974; WALTER & STADELMANN 1979).

According to OTTOW (1984) the amounts of copper, zinc and cadmium above tolerance thresholds block redox enzymes of ammonium and nitrite oxidation. BECK (1981) also found a reduced nitrification due to increased chromium and zinc concentrations and KLOSE (1993) mainly due to increased concentrations of lead.

In soils from the site KEL only a reduced nitrification occurred because of the contamination with chromium, copper, lead and zinc in connection with a very low pH of 3,8.

The behaviour of the cell-bound enzyme activities, dehydrogenase and DMSO reductases, determined in the wetland soils and in the urban soils of the Leipzig city was similar to the microbial biomass.

The cell-free enzyme activities of the alkaline phosphatase,  $\beta$ -glucosidase and protease is normally higher in the upper soil layers. Higher values of alkaline phosphatase in the deeper soil layer point to lower amounts of phosphorous in this layer. Higher values of protease and  $\beta$ -glucosidase point to an increased accumulation of mineralizable organic substance. Because of the relatively low contamination degree of these soils no significant effect on enzyme activities was found.

The results of the different parameters of soil biological activities showed that the occurrence and activity of soil micro-organisms is influenced by contamination levels only above a tolerance threshold. Effects of nutrients may overlay inhibition effects. An input of organic substances can reduce the bioavailability of heavy metals by complex forming reactions (KANDELER 1986).

### 3.2.4. CONCLUSIONS

From the investigations within this INTAS project including results from basic research in the institutes of the co-operators and from research activities on similar issues in other funded projects can be concluded:

The soils investigated showed very different degrees of contamination with heavy metals and organic pollutants.

The wetland soils were enriched with the heavy metals chromium, copper, lead and zinc as well as with organic chemicals. Main organic pollutant is the  $\beta$ -isomer of the hexachlorocyclohexane ( $\beta$ -HCH).

Despite of high total contents of heavy metals in some soils the contents of soluble or available (ammonium nitrate extracts, hot water extracts) forms of these elements is very low. This is probably due to inactivation by soil organic matter which results in low potential to be translocated to deeper soil layers. The formation of a pool of soluble copper, cobalt and zinc compounds depends on the amount of dissolved soil organic matter.

The contents of organo-chemicals, especially  $\beta$ -HCH, in the hot water extractable fraction of soil organic matter seem to provide a possibility for an evaluation of the behaviour (mobility and bio-availability) of organic pollutants in soil. The content of  $\beta$ -HCH in this fraction may contain up to 10 % of the total.

Granulodensimetric fractionations provide informations about of the preferred links of contaminants to specific soil fractions like mineral and humus complexes according to different stability and capacity of the bindings.

The heavy metal distribution in the granulodensimetric fractions reflects the order of the total content of heavy metals in soil. However, between the contents in the fractions large ranges are possible.

Most of the elements chromium, manganese, cadmium and cobalt were found in the coarse textured fraction and in clay (<1 µm).

The wide range of contamination degrees in the wetland soils are also found for organic pollutants in the granulodensimetric fractions. The high concentrations of organic chemicals in the clay fraction (<1µm) indicate the importance of adsorption processes to clay particles and stable bindings to complexes of clay and soil organic matter.

The biological investigations revealed that the biomass carbon is not related to soluble or total concentrations of heavy metals present in these soils. Contaminants above a tolerance threshold only will negatively affect the activities of micro-organisms. It is likely that the toxic thresholds of both heavy metals and organic pollutants have not been reached in these soils and that effects of nutrients may overlay inhibition effects.

### 3.2.5. PUBLICATION

As a result of this project one publication was prepared in co-operation of Russian and German scientists.

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E. Schulz and M. Körschens

Title: „About the distribution of heavy metals in different soil fractions as a criterion of their mobility as a risk for the environment“

In: Arch. Acker-Pfl. Boden. 19995, Vol. 39 pp 93-105  
Harwood Academic Publishers GmbH, Malaysia

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