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**CO-OPERATION PROJECT "FAST ON - SITE ANALYSIS by USING LOW - COST METHODS"** Influence of the mineralogical composition of contaminated soils, sediments and technical substrates on the elution- and extraction behavior of heavy metals and PAH

### **Axel Baermann**

Dr. Baermann & Partner, Mikroanalytik, Hochallee 40, D-20149 Hamburg, phone: 040 - 44 80 98 50, fax: 040 - 44 80 98 51, email: dr.baermann@t-online.de

#### Introduction

The fact that soil composition exerts substantial influence on the capacity of restraining pollutant of organic and inorganic compounds has been extensively described in literature. However, the influence of the soil matrix on the elution behaviour of heavy metals and the extraction of the PAH and their analyses has not yet been investigated in detail. It is still a matter of debate, which mineral or organic components have the largest affect on the extraction behaviour? The influence of smectites, active minerals, and other sorptive clay minerals as well as organic compounds on the extraction rate can be extremely high. In certain silty soils and clays only 60 percent of all hydrocarbons could be extracted by conventional techniques. Consequently, this can lead to a false evaluation of contaminated soils and its re-utilisation. Therefore, the main point of present investigation was to prepare different homogeneous types of soil standards and technical substrates for testing the influence of individual material compositions on heavy metal and PAH-

## Soil profile types in Germany



**River sediments and Holocene marsh** sediments (blue) in the area of Hamburg





**Profile type of Holocene Marsh** 



**Typical clayey marsh sediments** in southern Hamburg

extraction behavior.

#### **Sampling of PAH-contaminated soils**





Pumping out of tanks and excavation (gas factory)



Spoil of PAH contaminated soil and tails of concrete

#### **Coring of ash-contaminated soils**

Sampling sites



**Drilling and sampling of ash-contaminated substrates** (TS-RC 1)

#### Sampling of clayey marsh sediments Sampling of humous river sediments



Excavation of marsh sediments and tails of silt and clay (T1 / T2)

#### Humous river sediment in Hamburg-Neuland

#### **Sample preparations for mixing soil standards**



#### **Particle size distribution**

sample type	contamin. soil	sand	loamy sand	sandy Ioam	humous sediment	clayey silt	building debris
sample number	<b>B1</b>	<b>B2</b>	<b>B3</b>	<b>B4</b>	H1	T1	TS-RC1
Fractions in mm							
coarse sand (0,63-2,0)	11,2	7,4	1,3	3,1	15,1	0	21,6
medium sand (0,2-0,63)	35,1	58,9	32	27	31	0	40,4
fine sand (0,063-0,2)	26,3	20	30	31,3	18,4	3,5	18,6
coarse silt (0,02-0,063)	7,3	6,9	9,4	15,6	11,4	2,4	7,5
medium silt (0,006-0,02)	11,3	3,1	7,5	10,5	11,1	37,3	6,3
fine silt (0,002-0,006)	6,3	1,8	5,1	5	8,1	41,2	4,1
clay (<0,002)	2,5	1,9	5	7,5	4,9	15,6	1,6

#### **Microscopy and fractionation of different soil standards**







Sample of contaminated soil B1 (Hamburg-Bahrenfeld)

Clots of clayey loam with roots from holocene sediments (Hamburg-Allermöhe)



Fractions 2 – 4 mm of contaminated soil B1

Fractions 0.2 - 0.6 mm Fractions < 0.06 mm of Pb contaminated soil B5 of Pb contaminated soil B5 prepared for REM analysis

#### Geotechnical and sedimentpetrographical data

sample type	contamin.	sand	loamy	sandy	humous	clayey	building
	soil		sand	loam	sediment	silt	debris
sample number	<b>B1</b>	<b>B2</b>	<b>B</b> 3	<b>B4</b>	H1	T1	TS-RC1
water content, DIN 18128 [w-%]	19,9	1,2	8	5,3	12	10,1	1,2
loss of ignition, DIN 18128 [w-%]	2,8	1,1	5	2,1	28,8	3,8	2,7
loss of ignition, 1050°C [w-%]	4,1	1,4	5,4	2,8	31,9	14	5,9
lime content DIN 18129 [w-%]	0,5	0	0	0	3,2	10,9	3,8
total organic carbon [w-%]	0,8	0,5	2,17	0,71	29,5	0,6	1,8
fractions below <0,02 mm [%]	20	7	18	23	24	94	12
soil pH [-]	7	5,6	5,7	7,4	5,8	7,9	7,7
pH, after 48 h, [-]	7,5	5,8	6,2	7,4	6	8	7,9
conductivity, soil solution [µS]	1720	347	280	269	1520	520	2010
cation exange capacity [mval/100 g	4	5	11	11	2	25	2
max. watercapacity [g/100g TM]		28	50	37			
soil density [g/1000ml]	1605	1810	1050	1332	850	1030	1560
water absorbtion capacity [%]	30	35	45	40	5	50	30
(ENSLIN/NEFF; DIN 18132)							

#### **Preparing silt, clay and soil standards**



**Spiking soil standards with heavy metal solutions** 

**Homogenization of spiked standards** 

	type	quartz sand	quartz sand	sand	loamy sand	sandy Ioam	contam. sand	clayey silt	clayey silt
X	sample	<b>S</b> 3	<b>S</b> 3	<b>B2</b>	<b>B</b> 3	<b>B4</b>	<b>B</b> 5	T1	T1
	Pb								
	original content	< 20	< 20	< 20	< 20	< 20	78,5	< 20	< 20
The	spiked	770	717	776	771	759	-	-	779
	Cu								
	original content	< 20	< 20	5,1	< 20	< 20	18,2	< 20	< 20
NO.	spiked	549	515	505	530	501	-	500	484
O.	Zn								
	original content	< 20	< 20	24,7	< 20	< 20	81,9	< 20	< 20
	spiked	1222	1161	1295	1224	1368	-	1290	1233



Air dried samples of marsh (left) and river sediments (right) for spiking

#### X-ray diffraction analysis for clayey soils, silts and clays



### **REM- and EDAX analysis**

Quartz particles

without Fe-coating

without coati





#### **Original PAH-content in standards and after spiking**

type	contam. soil	sand	loamy sand	sandy Ioam	clayey silt	humous sediment	technical substrate	sand/ silt
sample	<b>B1</b>	<b>B2</b>	<b>B3</b>	<b>B4</b>	T1	H1	TS-RC1	M1
naphthaline								
original content	0,94	<0,003	<0,004	0,015	<0,3	<0,3	<0,3	<0,3
spiked	0,45	<0,3	<0,3	<0,3	0,96	2,01	0,36	<0,3
acenaphthene								
original content	0,86	<0,003	<0,004	<0,005	<0,3	<0,3	<0,3	<0,3
spiked	1,24	<0,3	0,89	0,45	2,38	2,88	0,99	1,08
fluorene								
original content	0,81	<0,003	<0,004	<0,005	<0,3	<0,3	<0,3	<0,3
spiked	1,54	0,38	1,53	0,71	2,72	2,84	1,42	1,32
phenanthrene								
original content	4,16	0,003	0,013	0,029	<0,3	<0,3	0,68	<0,3
spiked	3,24	1,72	2,57	1,39	2,94	3,09	2,82	1,64
anthracene								
original content	1,28	<0,003	<0,004	<0,005	<0,3	<0,3	<0,3	<0,3
spiked	2,14	0,74	2,21	1,21	2,65	2,6	1,9	1,52
pyrene								
original content	4,87	0,024	0,036	0,067	<0,3	<0,3	1,23	<0,3
spiked	3,76	2,59	2,71	1,6	3,02	3,44	4,33	1,42

sample type	contamin. soil	sand	loamy sand	sandy Ioam	humous sediment	clayey silt	building debris	silty clay
sample number	<b>B</b> 1	<b>B2</b>	<b>B</b> 3	<b>B4</b>	H1	T1	TS-RC1	T2
[in weigth-%]								
fractions < 2µm	3-5	2	5	8	5	15	2	30
sorptive clay minerals:								
smectite	<1	5	5-10	5-10	1-5		<1	20-25
kaolinite	5	5	10	10	5	20-25	5	20-30
illite	5-10	10	15	10	5	25-30	5	10-20
sorptive org. compounds	1	0,5	2	0,7	30	0,6	2	1-2
inert minerals:								
quartz	30-40	65-75	50-60	50-60	20-25	30-40	40-50	30-35
feldspars, silicates	5-10	5-15	0-5	0-5			5-15	0-5
anthropogen components	15-20				0-5		20-30	
(brick or concrete particles)								

Coating of particles with a Fe-Mn-Zn-Pb Matrix particle

**Fast method for quantification of active clays** by water absorption



#### **Results and conclusions**

- different profil types of northern Germany were standardized and could be sampled in different areas of Hamburg - 18 samples of standard soils, sands, loams, clays and technical substrates of different composition and grain size could be produced - geotechnical data, chemical composition and sedimentpetrographical/mineralogical data for all soil standards were determined - laser analyzed samples show higher concentrations of silt fractions as determination by DIN methods - basic materials were spiked with different heavy metals, both added in different concentrations - quartz sands, loamy sands, humous sediments, clayey marsh sediments, silty clays and technical substrates were spiked with PAH - best results for PAH-spiking could be reached by an acetone/water solution (40% / 60%) - content of sorptive and active clay minerals could be determined and quantified by x-ray diffraction analysis for all standards - coatings of FeOOH-compounds at quartz surface with pb-sorption could be detected by REM- and EDAX-analysis - content of organic compounds were measured by TOC-analyzer and could be differentiated by microscopic investigations - charcoal, tertiary brown coal, roots, organic matter or different humic acids could be differentiated by microscopic investigations - extraction and elution behaviour of heavy metals in sandy soils is reduced by Fe-coatings - elution of PAH in soils is strongly reduced by humic rich sediments and active clay components up to 30 % - the best method for fast and complete PAH extractions in field screening was an overhead shaker combined with an ultra sonic bath

- prepared soil standards make now possible, to calibrate and optimize the grade of retension and extraction behavior for each sample

**Microscopy for identifying inert components** in soil standards





**Preparing and separating contaminated construction waste for quantifying inert** components (concrete/debris, left) and sorptive coals and organic matter (charcoal, right)