EXPERIMENTS ON SPECIFIC RETARDATION OF SOME ORGANIC CONTAMINANTS BY SLURRY TRENCH MATERIALS

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INTRODUCTION

Slurry walls surrounding contaminated areas are important remedial measures for cleaning up improper hazardous waste sites. A comprehensive description of slurry wall application, configuration and construction was made by US EPA /1/. According to US EPA, slurry walls should have the following properties: low water permeability, resistance to hydraulic pressure and chemical attack. Our paper deals with an additional demand on slurry trench materials: they should exhibit high specific retardation of the movement of dissolved contaminants by sorption or irreversible chemical fixation.

Sorption results, when dissolved substances are concentrated at the solid-liquid interface. Two general cases of sorption can be distinguished: chemisorption and physisorption. The first, as due to coulombic attraction, ligand exchange or hydrogen bonding /2/, is characterized by high enthalpies of 60-200 kJ/mole. Desorption, on the reverse, requires activation energies exceeding the enthalpies of adsorption. If this energy is not available, sorption is irreversible /3/. An example is the strong and partially or fully irreversible binding of organic cations or basic compounds such as paraquat /4/ or triazine herbicides /5/ on clays or humic substances. The other general case of sorption is that of physisorption, which is due to the much weaker van der Waals forces. Enthalpies of adsorption are only in the range of 1 to 2 kcal/mole /6/, and sorption can easily be reversed by addition of small amounts of energy (e.g. by dilution).

Sorption studies are conducted by equilibrating known amounts of solids with solutions of the contaminants to be examined. Usually sorption is described by isotherms. The amount of sorbate being sorbed is determined in relation to the concentration of the chemical of interest in solution at equilibriun. Several models describe this relationship. The empirical Freundlich isotherm

$$q_e = K_F \, C_e^{\frac{1}{n}}$$

in most cases describes adequately the sorption of organic compounds from water onto solids (q_e: amount sorbed; C_e: concentration of compound in solution; K_F and n empiric constants).

In many cases the term 1/n equals or is near to 1, and the isotherm gets the form

$$q_e = K_p \, C_e$$

where K_p is termed the partition coefficient. This model is that of linear adsorption or constant partitioning.

Slurry trench materials usually consist of bentonite, cement, sand and in some cases of additional inert fillers, thinners and dispersing agents, flocculants and polyelectrolytes, and chemical additives. The slurry formulations of this paper were developed by the Institut für Grundbau und Bodenmechanik, Hannover, Prof. Dr. Müller-Kirchenbauer. They were optimized with respect to non-permeability and construction requirements.

The sorption of organic chemicals on solid surfaces is dependent on their functional groups, the size and shape of the molecule and - if there is any - their charge. Based on this properties, the following categories can be set up:

(i) Cationic or basic compounds. They interact with negative charged clay particles and are strongly or irreversibly bound. They have not been tested here.

(ii) Acidic compounds. They are repelled by the negative charge of clay or organic material and therefore any adsorption is hardly to be expected. The herbicides 2,4 D and 2,4,5 T (phenoxy acetic acids) were used in our experiments.

(iii) Non-polar, volatile substances, mainly used as dissolving agents. They interact by hydrophobic bonding. Only weak adsorption on sediments and soils have been observed. Toluene was tested here.

(iv) non-polar, non-volatile substances. The hydrophobic bonding forces are much stronger than in the latter case, increasing with decreasing water solubility. On soils and sediments organic matter is the main adsorbent. We tested (in decreasing order or water solubility given in brackets): Parathion (21 mg/l), (-HCH (7 mg/l), HCB (5 µg/l), and pp'DDT (1.2 µg/l).

MATERIALS AND METHODS

Batch equilibrium experiments were conducted using C-14 labelled toluene, parathion, hexachloro benzene and 2,4-dichloro phenoxy acetic acid. They were dissolved in distilled water to about half or their solubility and diluted in the order 1:2:4:8:20 or in some cases 1:5:25. 25 ml or these solutions were transferred into centrifuge vials containing 0.1 (strong) sorbing media) to 10 g (weak sorbing media) of solids (triplicates). The vials were glass stoppered and shaken over head for 20 hours. Then the vials were centrifuged, 5 ml of the supernatant was taken off and the activity determined by liquid scintillation counting. Further 15 ml of water were taken off and discharged, and the vials were refilled with distilled water to 25 ml and shaken again for 20 hours for consecutive desorption determination. After the last desorption step (or, if no desorption was conducted, after the adsorption), instead of water, the vials were refilled with 20 ml of an non gel building scintillation fluid, which was added to extract radioactivity from the solids. The probe was treated with ultrasonic, centrifuged and the activity in the supernatant measured. Pretests showed a good extraction efficiency (>90%).

Thin layer chromatography was conducted according to Helling /7/ and Poon /8/ using slurry components or mixtures as liquid phase. The solids were spread as a 0.25 mm layer on 20 x 20 cm glass plates. The chemicals of interest were spotted as usual and the chromatogram developed in a TLC - water tank until the water front had reached about 10 cm. This took half an hour to some hours. After development, the plates were air-dried. Detection of the chemicals was made by (i) several spray reagents, and (ii) autoradiography, using radiolabelled compounds. The best spraying method was application of a solution or 1 g $AgNO_3$ plus 5 ml of conc. ammonia, filled up to 100 ml with ethanole. After spraying, parathione sometimes becomes yellow or, as the other, the chlorinated compounds, after irradiation with uv, becomes gray. Some plates had to be irradiated for a very long time (40-65 hours). For the autoradiography, a Kodak XAR5 X-ray Film was used. Time of exposure was 24 hours. The activity of the compounds was about 20 nCi.

TABLE 1. pH and of the slurry organic matter content slurry components and formulations used

	pH	0.C. %
Ground Quartz	6.2	0.00
Cement, H0Z 35	12.7	0.00
Fly Ash	11.5	2.80
Ground Slate	7.8	0.31
Na-Bentonite	9,6	
Ca-Bentonite	7.1	0.00
"white" Clay	6.1	0.09
"Blue" Clay	6.2	0.86
"Green" Clay	8.0	0.08
Slurry mixture DW 2	9.8	0.07
Slurry mixture DW 4	11.9	0.01
Slurry mixture DW11	10.0	0.07
Slurry mixture DW13	10.6	0.48

The sorbents used are given in Table 1, including their organic carbon content and pH (measured in an 0.01 m CaCl solution at a solution/solids ratio of 1:2,5). The slurry wall formulations are compiled in Table 2. The mixtures were prepared according to the protocols of the Institut für Grundbau und Bodenmechanik, Hannover. The additive DYNAGROUT® T is an alkali aluminate, DYNAGROUT® SP an organo-Silane /9/ both from Dynamit Nobel, Troisdorf. To produce a spreadable mixture for TLC, the water content was increased to 50% (DN 05A: 40%) while the interrelations of the other components were the same as in the formulation protocols.

TABLE 2. Composition or the slurry wall formulations (developed by Institut für Grundbau und Bodenmechanik Prof. Dr. MüllerKirchenbauer, Hannover).

	DW 02	DW 04	DW 11	DW 13	DW 22	DW 23	DW 05A
Water	40.6	40.8	32.6	37.7	21.4	38.8	19.4
Ca-Bentonite	10.2	10.4	5.2	9.4	4.5	3.9	
Cement, HOZ 35	4.6	4.7		8.6		3.9	
“White” Clay	4.6	11.1	5.2	4.3	4.5		36.5
Fly Ash				17.1			
Ground Slate	20.0		22.1		19.3		
Ground Quartz	20.0	32.0	26.0	22.9	34.1	51.8	43.3
Dynagrout© T							0.25
Dynagrout© SP					2.4	1.6	1.0
Na-Aluminate			1.0				
Na-Water Glass			7.9		13.8		

RESULTS

Batch equilibrium experiments

HCB, in accordance with its low water solubility, exhibited the highest sorption throughout. With the exceptions of ground slate, fly ash and the slurry formuLations DW 4, DW 11, DW 13, linear sorption isotherms are well approximating their sorplive behaviour. Sorption of HCB from the slurry components was generally reversible. Quartz, however, showed a marked irre-

TABLE 3. Partition coefficients (µg sorbate/g of soil per µg of sorbate/g of solution at equilibrium) for HCB, parathion and toluene on different slurry components and formulations. (Batch equilibrium experiments. Water solutions of 0.1 to 5 µg/l HCB, 0.5 to 15 mg/l parathion and 1 to 50, in some cases up to 200 (ground slate) mg toluene. n.l. means no linear sorption, n.s. no measurable sorption.

Sorbens	Sorbens conc. [g/l]	HCB				Sorbens conc. [g/l]	Parathion				Sorbens conc. [g/l]	Toluene			
		$K_p$min	$K_p$max	$K_p$mean	± s		$K_p$min	$K_p$max	$K_p$mean	± s		$K_p$min	$K_p$max	$K_p$mean	± s
Qartz	1000	1.2	4.3	2.8	0.6	40	0.23	1.5	0.74	0.44	250	n.s.	n.s.		
Quartz + 1% Na-Aluminate	40	2.7	8.5	4.4	1.8	40	< 0	0.9	0.35	0.37	40	n.s.	n.s.		
Quartz + 1% Dynagrout T	40	2.8	6.2	4.2	1.1	40	n.s.	n.s.			40	n.s.	n.s.		
Quartz + 1% Dynagrout SP	40	63	96	73	10	40	0.4	5.3	2.7	1.7	40	n.s.	n.s.		
Ground Slate	2.5	5200	12500	n.l.		4	34	124	n.l.		125	0.5	96	n.l.	
Fly Ash	4	6150	15890	n.l.		40	3.7	17	n.l.		50	1.4	11	n.l.	
Cement (HOZ 35)	40	24	35	29	4.1	40	0.07	0.50	n.l.		80	n.s.	n.s.		
Na-Bentonite	25	47	350	132	70	40	4	18	12	3.6					
Ca Bentonite	25	61	79	68	5.3	40	13	17	14	1.4	80	0.1	2.6	n.l.	
Clay "white"	25	50	114	88	18	40	2.0	3.4	2.6	0.50	50	0.4	1.4	0.8	0.4
Clay "Green"	40	1060	1640	1320	150	40	42	65	48	8.0	50	n.s.	n.s.		
Clay "Blue"	40	860	1130	990	80	40	35	24	27	5.0	50	2.6	3.8	3.0	0.5
Formulation DW 2	40	1040	2410	1750	530	40	10	76	n.l.		200	0.5	2.4		
Formulation DW 4	40	26	64	n.l.		40					200	0.2	0.4	0.27	0.06
Formulation DW 11	4	830	2480	n.l.		40	14	224	n.l.		40	0.6	4.0	n.l	
Formulation DW 13	40	412	736	n.l.		40	2	21	n.l.		200	0.2	0.8	0.5	0.23
Formulation DW 22	4	760	1040	940	100	40	13	59	n.l.		200	1.4	3.6	2.2	0.8
Formulation DW 23	4	904	1574	1248	241										
Formulation DW 05A	4	47	70	55	7	40	1.4	3.9	2.8	0.9	200	0.2	0.5	0.3	0.1

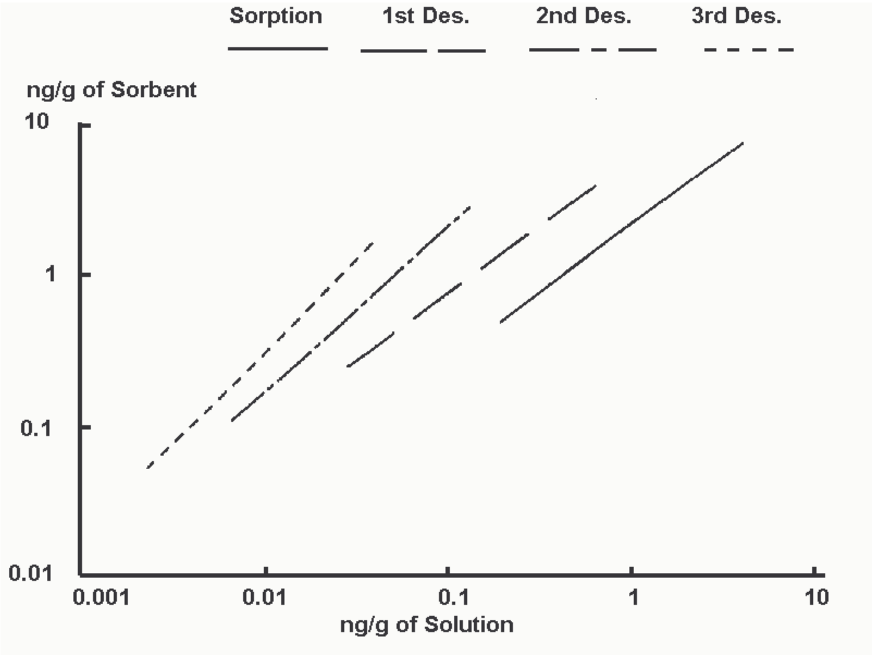

Fig. 1: Sorption and desorption: HCB on quartz. Freundlich plots of sorption isotherms

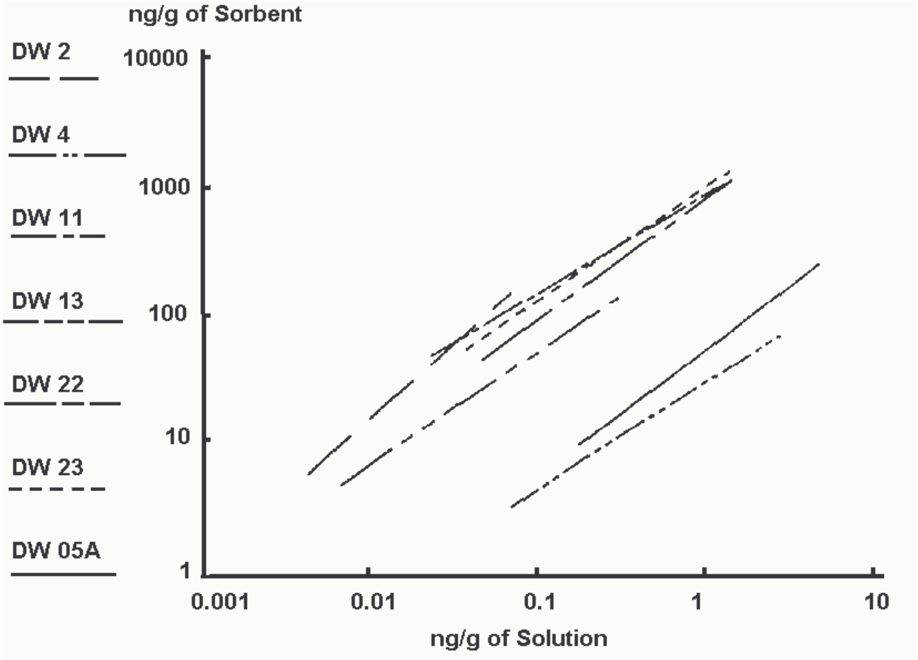

Fig. 2: HCB on slurry trench materials. Freundlich plots of sorption isotherms

versibility (Fig. 1). Quartz, on the other hand, had the lowest K_p value (2.8; ng sorbate/g of soil per ng of sorbate/g of solution at equilibrium). An other weak sorbent was cement, HOZ 35 (K_p=29). Two groups of clay can be stated: the low sorbing bentonites and the "white"clay (K_p about 100) and the "green" and "blue" clays with tenfold higher partition coefficients. The highest partition exhibited ground slate and fly ash, both in the range of 5000 to 15000. Aluminate-treated quartz showed no better sorption than quartz alone. The silane DYNAGROUT® P, however, increased the sorption of quartz more than 2O-fold.

Two groups of slurry mixtures can be established (Fig. 2). DW 4 and DN 05A, both containing neither fly ash nor ground slate, are weak sorbents (K_p in the order of 50), while the other had K_p-values in the order of 1000. Parathion has a relatively high solubility, and the sorption is therefore much less than HCB. While quartz and the clays followed a linear adsorplion isotherm, cement, ground slate and fly ash did not and their sorptive behaviour is better to be described by the Freundlich-equation. Decreasinq the adsorbate concentration increases the partition values. The sorption isotherms of the slurry mixtures DW 4 end DW 05A were linear, the other were not. While the desorption of ground slate, fly ash and cement seemed to exhibit a slight irreversible component, desorption of the other components was reversible.

The best sorbent, as in the tests with HCB, was ground slate, with a K_p-span from 34 to 124. It was followed by "green" clay ($K_p$max=65), "blue" clay (35), Na- and Ca-Bentonite (18 and 17, resp.). Fly ash, whose sorption of HCB was about equal to the best, ground slate, exhibited only a medium sorption of parathion. Quartz, aluminate treated quartz and cement as well as "white" clay are only very weak sorbents. DYNACROUT® SP enhanced sorption of quartz only about 3-fold. The slurry formulations DW 4 and DW 05A, as in HCB, are also very weak sorbinq media. On the other hand, K_p-values of parathion on the other mixtures are in the magnitude of 100.

Toluene was chosen as an extreme, because of its expected very low sorption on mineralic materials. Ground slate, however, had remarkably high partition coefficients. The sorptidn followed the Freundlich isotherm and ranged from K_p=0,5 (sorbate concentration: 227 mg/l) to 96 (sorbate concentration 4.1 mg/l). Fly ash exhibited similar properties with K_p-values from 1.4 to 10.8. "Blue" clay had a maximum K_p of 3.8, Ca-bentonite of 2.6 and "white" clay of 1.4. The other components showed no sorption.

The slurry mixtures are generally weak sorbing media according to toluene. The partition coefficients are below 5, in the ease of DW 4 and DW 05A even below 1, what means, that on unit weight basis there is more toluene in solution than sorbed.

2,4-D was tested only on quartz, ground slate and "white" clay. As 2,4-D is an acid, pH seemed to be an important factor in sorbing behaviour of this compound. Therefore the batch equilibrium experiments were conducted with different pH ranging from 1 to 12. In each case no sorptton of 2,4-D on quartz and ground slate could be detected. A weak sorption, however, (K_p about 0.5 to 1) could be seen on "white" clay at pH of 1 and 2.

Thin layer experiments

The non-polar compounds pp-DDT, HCB, y-HCH and parathion showed no migration in these experiments. Only in the case of using autoradiography, as a very sensitive detection method, it seemed, that some migration of a small amount of these sorbates could have happened (Fig. 3, DW 13). On the

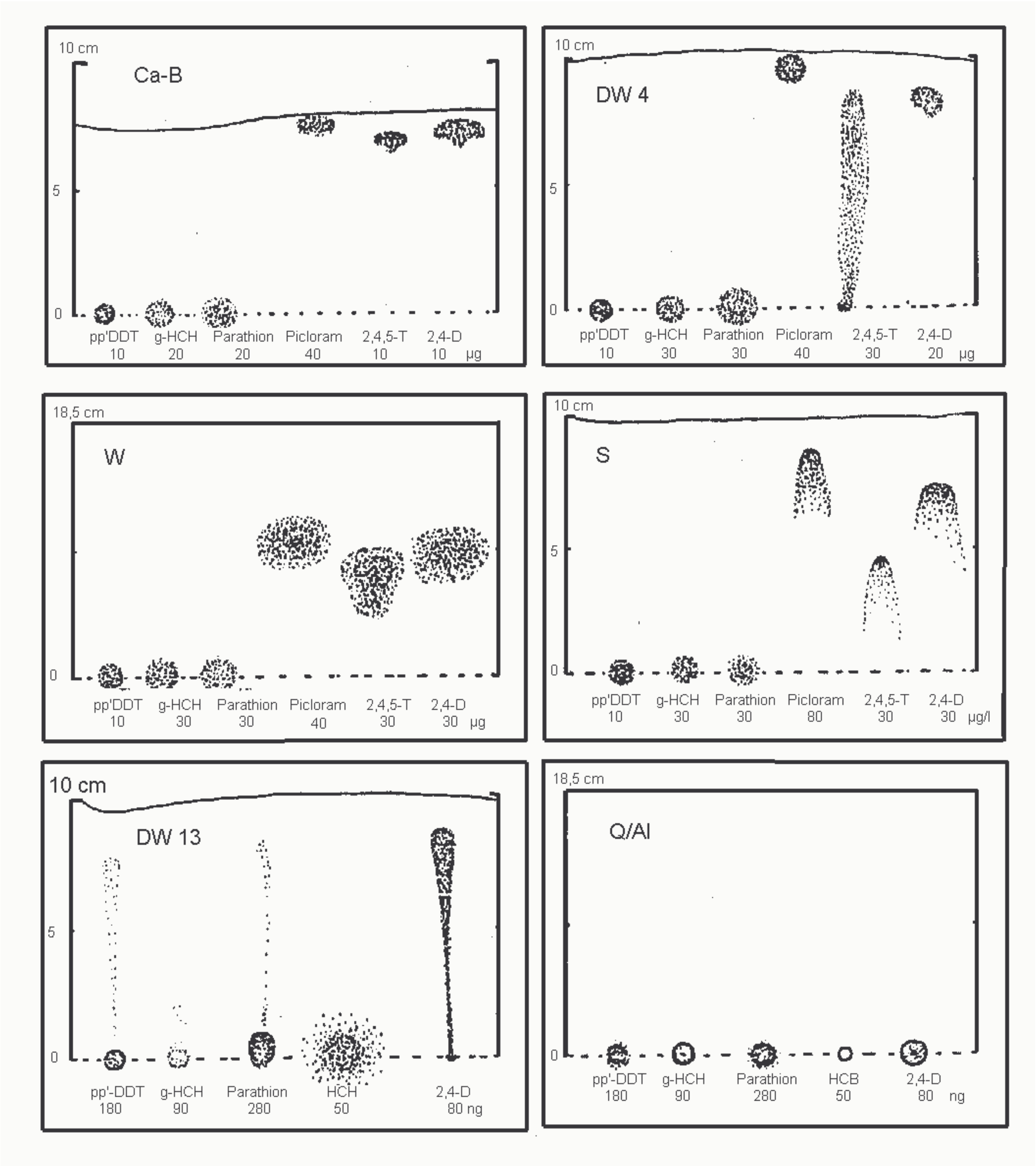

Fig. 3: Thin layer chromatograms of diverse sorbates on slurry trench components or formulations. - Ca-B: Ca-bontonite. DW 4: Slurry mixture 4. W: "White" clay. S: Ground slate. DW 13: Slurry mixture 13. Q/Al: Na-aluminate treated quartz. Detection mode: Ca-B, DW 4, W, S: by spraying, DW 13, Q/Al: by autorodioqraphy.

other hand, the acids picloram, 2,4-D and 2,4,5-T exhibited high RF-values (that is the relation of the frontal distance of the spot to the distance of the water front from the start). From the slurry components, only "white" clay and ground slate retained the acids to a remarkable extent (Fig. 3). While in the case of "white" clay the spots wandered unchanged in shape, in ground slate some "tailing" can be observed. This indicates an irreversible component in sorption/desorption of the acids on slate.

This effect is much more pronounced in the case of cement, HOZ (which equals the behaviour on DW 4, Fig. 3): 2,4,5-T shows a considerable tailing, while picloram as well as 2,4-D don't do so. Migration was fully inhibited, if aluminate treated quartz was used (Fig. 3: Q/Al).

The slurry mixtures DW 2, DW 4 and DW 13 were quite similar to cement, and did not differ in their sorbing properties (Fig. 3: DW 4). On the other hand, DW 22, a silane treated slurry, completely retained the herbicide spots.

DISCUSSION AND CONCLUSION

As shown by several workers, for soils and sediments organic matter content is the "master factor" influencing sorption behaviour of non polar organic substances /9/. This seems not to be true for our experiments. Fly ash, for example, is the best sorbing medium for HCB (OC: 2.8%) and has the highest amount of organic carbon. On the other hand, fly ash had the same sorbing properties for parathion as Ca-bentonite, which contains no organic carbon at all. Ground slate, having only about one tenth of the organic carbon of fly ash, sorbes HCB in the same amount as fly ash and parathion is even sorbed 5- to lOfold more. "Blue" and "green" clay exhibit the same sorption of HCB and parathion, but have 0.86 resp. 0.08% OC content. Further mineralogical analyses will probably give some clarification of the reasons of these differences in sorptivity.

Our investigations showed that, if possible, as inert fillers ground slate should be given preference over quartz. Cement should be minimized, while fly ash shows good properties. Aluminates did not show any effect on sorption of non polar substances. The silane DYNAGROUT SP enhanced sorption of non polar substances on quartz. Both reactives seem to be effective in inhibiting migration of organic acids.

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