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Reactions of hydrocarbons during thermodesorption from sediments

Frank-Dieter Kopinke*, Matthias Remmler

Department of Remediation Research, Centre for Environmental Research Leipzig-Halle Ltd., Permoserstrasse 15, D-04318 Leipzig, Germany

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Abstract

Thermal reactions of hydrocarbons, which were loaded onto a river sediment, were investigated at 300°C in an open and in a closed reactor. The results give evidence that the thermodesorption of PAHs and hydroxylated aromatics is accompanied by their chemical conversion to non-volatile products, which can be called charring. Quartz powder as an inert carrier does not effect such reactions. The rank in reactivity observed for charring of PAHs is consistent with their reactivity in radical reactions. The sediment ash is more active in hydrocarbon conversion reactions than the native sediment. This points to the mineral matrix of the sediment as the actual carrier of the catalytic activity rather than the sediment organic matter.

Keywords: Sediment; Organic pollutant; Thermodesorption; Thermal reaction; Charring

1. Introduction

Organic pollutants in mixed solid matrices, such as soils or sediments, are bound mainly to the polymer organic matter. They can be adsorbed on the surface of particles or dissolved in the humin-like organic phase. The latter state will dominate the sorption of hydrophobic compounds on materials rich in organic matter after a long incubation time. The limited accessibility of pollutants in this dissolved state renders it very difficult to remove or degrade them without destroying the material, e.g. by combustion. Microbiological and most of the chemical remediation techniques need direct contact between the pollutant molecules and a reactive species, such as microorganisms, enzymes or chemical oxidizing agents. In this way, the slow intraparticle diffusion of the pollutant can determine the rate of the cleaning process. Therefore, the idea to stimulate detoxifi-

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* Corresponding author.

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tion inside the solid matrix is tempting. What methods are, in principle, available to hieve this aim? The initiation of chemical reactions needs catalysts or some energy pply. The introduction of any catalyst is restricted by the transport limitations men- ned above. Hence, the only way to stimulate chemical reactions inside a given solid itrix is the supply of energy. This can be done, e.g. by means of γ-radiation or by heat ut. A recent review on soil in situ heating technologies was published by Houthoofd et [1]. One of the promising techniques is microwave or radio-frequency heating, which rmits temperatures up to about 300°C [2–5].

When volatile compounds in a sorbed state are heated, they can be desorbed into the s phase or they can be converted by thermally initiated chemical reactions. As a rough proximation, we consider these pathways to be a mainly physical and a chemical proc- , respectively [6]. The result of the competing processes depends on many parameters, ne of them are the volatility of the target compound, its chemical reactivity, the ap- ed heating rate, transport conditions (porosity of the carrier, gas flow) and, finally, the ivity of the matrix.

Low-temperature thermal treatment processes (LTTP) play an important role among so-called innovative technologies for cleaning up hazardous waste sites [7]. Gener- y, the thermodesorption of volatile pollutants out of the soil is the desired result [8–]. Sometimes, semivolatile compounds were found to be at least partially removed o, but they could not be detected among the recovered desorption products [14,15]. is indicates a chemical conversion, either by pyrolysis, hydrolysis or by oxidation ing place during the thermal treatment. Part of the target compound may be degraded, ducing volatile fragments, another portion can form bound residues, which are cova- tly bonded to the soil organic matter (SOM). The aspect of chemical reactions during v-temperature soil treatment has not attracted much attention until now, possibly be- se it was mainly a domain of engineers rather than of chemists [16–18].

It is noteworthy that a microbial treatment of contaminated soils reaches a similar re- t. Besides simple degradation products (finally water and carbon dioxide), biomass l bound residues are built up [19,20]. The latter process is called humification. Decon- nination of polluted sites by humification is an interesting, but controversial remedia- n strategy.

The corresponding thermal process is charring [21–24]. Natural biopolymers, such as bohydrates, lignin and humic substances contain a lot of functional groups, which are rmally labile. After splitting off fragments, a residue rich in carbon and depleted in lrogen and oxygen, called char, is left. The thermal degradation of SOM starts at ut 100°C (cf. Fig. 1). The mechanism of its pyrolysis is very complex, and it is not understood in detail [25,26]. Molecular, radical and ionic reactions are assumed to ceed simultaneously. The main point is the following. During the course of pyrolysis, y reactive species are formed, which may be able to attack the adherent pollutant lecules. Even if these are thermally very stable like, e.g. PAHs [27–29], they can be olved in radical-molecule reactions, which can be a hydrogen abstraction or a radical lition, followed by the formation of new covalent bonds between pollutant molecules l the polymer matrix. Thereby, the backbone of the pollutant molecule need not be troyed. The rate of bimolecular reactions, however, strongly depends on the mobility both the participants. Although in solution the reaction rate may be sufficiently high, in a solid matrix like SOM a radical chain reaction is transport-limited [30]. Nevertheless, looking at pollutants dissolved in a matrix of polymer organic material, there is a good chance that those compounds not desorbing fast enough can be buried by thermally initiated reactions [22]. In contrast to reagents from the outside, the reactive intermediates are generated just inside the SOM, i.e. very close to the pollutant molecules. Beside SOM, the mineral matrix of the sediment may possess catalytic activity, which is attributed mainly to clay minerals and possibly to some metal oxides [31,32].

The low-temperature treatment of soils ($T \leq 300°C$) has, with regard to the properties of the cleaned material, some advantages over the more severe thermal processes, such as medium-temperature pyrolysis ($T \geq 500°C$) and combustion. The original organic carbon, many functional groups and the grain structure of the soil survive. However, the pyrolysis of SOM is always accompanied by a new formation of tar components to a certain extent. For this reason, the treatment temperature is to be kept as low as to be still sufficient for reaching the decontamination aim.

Our interest is focused on the interactions at elevated temperatures between volatile hydrocarbons, such as PAHs and phenols, and a sorbent that is representative of natural materials. As sorbents we chose a fine fraction of a river sediment rich in organic matter and the corresponding sediment ash.

2. Experimental

The target compounds (see Tables 1 and 4) were commercially available (purity >98%) and were used as received.

The sediment sample was taken from the river Weisse Elster near the town of Leipzig. The sample was air-dried and sieved. The size fraction <63 μm (10 wt% of the whole sample) was used for all the pyrolysis experiments. The following properties were determined: moisture (105°C) 3.0 wt%; organic matter (1 h, 550°C in air) 15.4 wt%; elemental analysis (dry sample, LECO CHN-932) 7.45 wt% C, atomic ratios H/C = 2.00, N/C = 0.06, S/C = 0.04; surface area (BET-method, ASAP 2000) 10 $m^2\ g^{-1}$ (14.5 $m^2\ g^{-1}$ for the corresponding sediment ash); pore volume (2–150 nm) 45 $mm^3\ g^{-1}$ (60 $mm^3\ g^{-1}$ for the corresponding sediment ash), maximum of pore-size distribution at 3–4 nm.

A detailed thermoanalytical characterization of sediment samples is given elsewhere [33]. Fig. 1 presents three thermograms obtained with a Shimadzu TGA-50 thermobalance that was on-line coupled with a GCMS-QP1000EX quadrupole mass spectrometer. The DTG curve and the total-ion-current (TIC) curve of the mass spectrometer are quite similar. The "organic" TIC curve (dashed line, TIC minus signals of inorganic components, such as water and carbon oxides) gives a clear picture of the temperature range, where the production of pyrolysis fragments starts. This temperature is about 150°C for most of the products. The decomposition of the SOM is completed at 600°C (He flow, 0.1 MPa, $\dot{T} = 10\ K\ min^{-1}$).

We used a fine quartz powder (<50 μm, 1.2 $m^2\ g^{-1}$) as a reference material. The impregnation of sorbents with sorbate compounds was performed according to the following procedure: About 100 mg of the carrier were suspended in 100 μl of n-hexane that contained the sorbate compounds in defined concentrations (e.g. 100 ppm per compo-

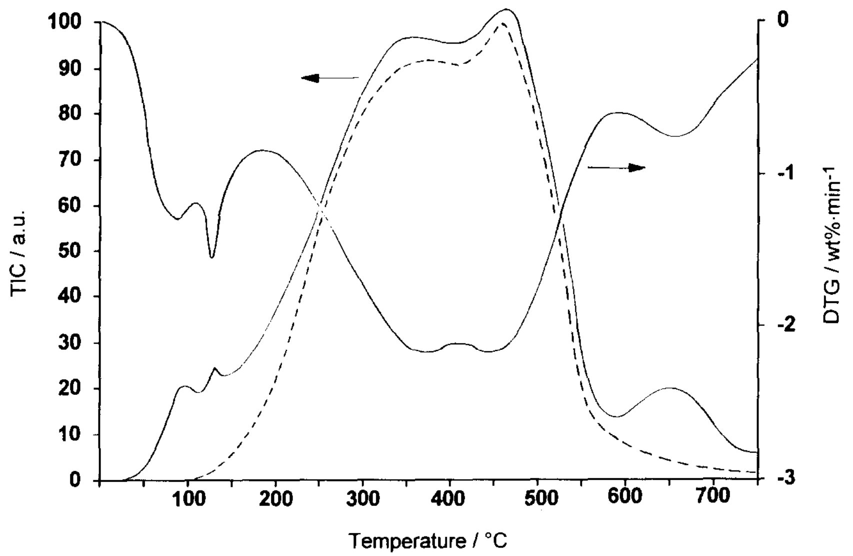

Fig. 1. TG-MS analysis of a sediment sample ($dT/dt = 10$ K min^{-1}, mass range 10–300 amu, 30 ml min^{-1} He flow).

nent). Then the solvent was carefully evaporated under a slight flow of nitrogen, partial reflux (micro air cooler) and ultrasonic treatment. The final bath temperature was not allowed to exceed 80°C. When the solid residue became powdery again, the procedure was stopped and the flask was tightly closed by a glass stopper. This way the evaporation losses during the impregnation procedure of compounds having boiling points >200°C could be kept low, but they could not be avoided completely. The storage time of the sample between impregnation and thermal treatment was about 24 h.

The impregnated sorbent was submitted to a thermal treatment in two different ways. One way was a pyrolysis-GC procedure, i.e. a thermodesorption under flow conditions. About 5 mg of the sample were placed in a quartz tublet (10 × 2 mm), which was positioned in the platinum coil heater of a flash pyrolyzer (CDS Pyroprobe 1000®). The coil element of the pyrolyzer was inserted into a heated interface (250°C) arranged directly above the injector of a GC (DANI 86.10). The pyrolyzer interface and the GC injector were connected by a short steel capillary. The pyrolysis of the sample was triggered off immediately after closing the interface. A shortcoming of this device consists of an unavoidable loss of highly volatile compounds during the insertion step (≤ 10 s), when the sample is already heated up in the interface, but the carrier gas flow still purges the interface to the atmosphere. The pyrolysis conditions are specified by the set temperature of the pyrolyzer and the pyrolysis duration. The standard conditions of thermodesorption (400°C, 15 s) were chosen in such a way that only few hydrocarbon products were formed by the pyrolysis of the native sediment. A heating time of 15 s was found to be sufficient. Doubling of the heating period did not influence the result significantly.

A careful temperature calibration by means of a thin thermocouple ($d = 0.2$ mm) revealed that up to 600°C the actual temperature was about 15 ± 5 K below the set value.

At higher temperatures the deviation between the two temperatures increased (up to 60 K at 800°C). The actual heating rate of the sample depended on the final temperature. The higher the set temperature, the higher the initial heating rate. The pyrolyzer needs 5–6 s to reach 90% and 10–12 s to reach 99% of the final temperature, respectively. A similar behaviour of a Pyroprobe® pyrolyzer was described elsewhere [34].

The GC conditions were as follows: capillary column 50 m NB-54 (i.d. 0.32 mm, film thickness 0.25 μm), temperature program 10 min 40°C, 4 $\mathrm{K\,min^{-1}}$, 30 min 285°C, carrier gas He, split 1:75, FID. The quantitative result of a thermodesorption run is given in terms of % recovery based on the GC analysis of the hexane starting solution. Thereby, one component, usually a n-paraffin, was taken as an internal standard, the recovery of which was assumed to be 100%.

The second method of treatment was pyrolysis in a closed system to prevent the escape of the target compounds from the reaction zone. About 20 mg of the impregnated sorbent were placed in a glass capillary ($50 \times 1.6 \times 0.16$ mm^3). The ends of the capillary were blocked with quartz wool and sealed under a slight flow of helium. Then the capillary was put into a copper tube and exposed to the thermal treatment in a muffle furnace (±5°C) for a certain period (10 min to 24 h). After cooling, the capillary was weighed to verify its tightness and opened by cutting off both ends. Then the treated sample was extracted by slowly running 0.5 ml of a benzene–acetone (1:1) mixture through the capillary, which was placed in an ultrasonic bath for 30 min. The extract was collected in a 1 ml vial without having any contact with materials other than glass. After adding 100 μl of a standard solution containing an external standard (usually a n-paraffin), the extract was analyzed by GC under the conditions described above without performing any clean-up. Additionally, a static extraction of samples with benzene–acetone mixtures under ultrasonic treatment was carried out. The results of both procedures were similar. The recovery rate of most of the hydrocarbons for blank experiments, i.e. impregnation and extraction without thermal treatment, was in the range of 80–100%, except for methylanthracene and naphthols, a portion of which was sorbed irreversibly on sediment ash at 20°C.

3. Results and discussion

Thermodesorption in the Pyroprobe® device can be considered as roughly representative of a fluidized bed reactor with respect to the fast heating up, a short residence time and flow conditions. Table 1 presents the results of thermodesorption experiments as rates of recovery.

The 20 sorbate components are listed in the order of increasing boiling points. They cover the range from 180 up to 350°C. The scattering of the recovery rates amounted to ±5 to ±10% (relative); the latter value applies to the highly volatile compounds. The data given in Table 1 are mean recoveries from three runs each. In the cases of only weak interactions between carrier and sorbate, any open handling of the sample gave rise to losses. This is the main reason for incomplete recoveries from quartz powder, which is most obvious for the homologous series of paraffins (recoveries from 47% for C_{11} up to about 100% for C_{20}).

Table 1

Thermodesorption of hydrocarbons from different sorbents (contamination 100 ppm of each component, 15 s, 400°C), data as recovery rate in %

Component	b.p./°C	Quartz powder	Sediment	Sediment ash	Domestic ash
Phenol	181	n.d.	35	16	n.d.
n-Undecane	196	47	81	90	70
p-Cresol	202	n.d.	22	<1	n.d.
Nitrobenzene	211	n.d.	31	56	n.d.
2,4-Dimethylphenol	212	100	50	<1	<1
4-Chlorophenol	217	n.d.	30	2	n.d.
m-Nitrotoluene	231	96	53	67	45
Methylundecanoate	248	109	17	<1	<1
n-Tetradecane	252	67	91	104	97
1-Tetralone	257	n.d.	71	48	n.d.
2,3-Dimethylnaphthalene	260	80	85	46	89
n-Octylbenzene	263	87	92	75	94
1,2-Dimethylnaphthalene	266	79	84	48	104
n-Pentadecane	270	75	100[a]	100[a]	100[a]
1-Naphthol	279	95	<1	<1	<1
n-Hexadecane	283	82	93	86	91
n-Heptadecane	302	89	87	75	82
Phenanthrene	340	103	84	38	60
Anthracene	342	103	63	11	52
n-Eicosane	350	100[a]	75	40	50

[a] This component was chosen as the internal standard.

The sediment is a better sorbent for hydrocarbons. The polar compounds were desorbed incompletely. Naphthol was detected in the thermodesorbate as trace only. In order to distinguish between evaporation losses during sample preparation and incomplete thermodesorption, it is suitable to take the recoveries of n-paraffins as a criterion. Paraffins can be assumed to be less reactive sorbates. Hence, their recoveries are controlled mainly by physical effects. Fig. 2 presents recoveries of paraffins from the different sorbents.

Active sorbents, such as the sediment and even more pronouncedly the ashes, give rise to losses of high-boiling paraffins. Possibly, this is due to the cracking of paraffins, which do not escape from the heated sample fast enough. A homogeneous gas-phase cracking is too slow [35,36] to explain the observed conversion degrees, but inorganic materials are known to catalyze cracking. Although we did not perform detailed product analyses, no prominent single new peak could be observed in the thermodesorption chromatograms among the sorbate components.

The tricyclic aromatics phenanthrene and anthracene are a suitable pair of sorbates having similar physical but different chemical properties. A significant difference in the recoveries of both these compounds definitely reflects the occurrence of chemical reactions. Thus, the loss of 37% of anthracene in comparison to only 16% loss of phenanthrene after thermodesorption from sediment is to be attributed to chemical reactions.

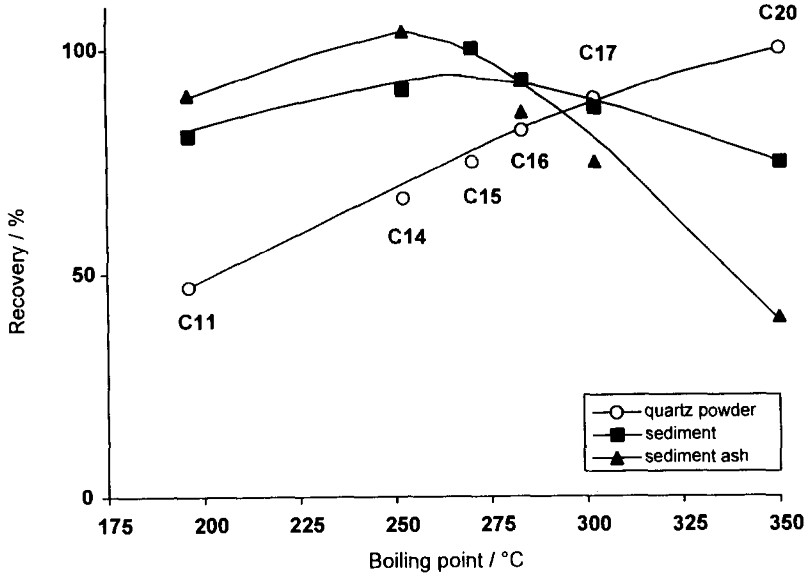

Fig. 2. Thermodesorption of paraffins from different sorbents (contamination 100 ppm of 15 components each, 15 s, 400°C).

The ashes are more active sorbents than the native sediment. The phenols and the ester were almost completely removed from the thermodesorbate. Even the PAHs free of any oxygen-containing groups are considerably depleted. The rank of conversion (53% for dimethylnaphthalenes, 62% for phenanthrene, 89% for anthracene on sediment ash) is consistent with the knowledge of the chemical reactivity of PAHs [28,29,37–39].

The high reactivity of methylundecanoate is surprising in so far as its alcoholic chain, the methyl group, does not possess a β-C–H bond, which is a condition of the *cis*-elimination as the preferred ester-pyrolysis mechanism.

Domestic ash is less active than sediment ash. This is due to the high temperature during the burn-off of the lignite that deactivates the ash. A high temperature treatment (900°C for 1 h) strongly reduces the activity of the sediment ash.

The sediment ash was involved in the thermodesorption experiments as a possible surrogate material of the inorganic sediment matrix. Although moderate burn-off conditions (550°C) were applied, the original inorganic matrix changed its properties significantly. Its observed high activity may be due to defects in the crystal lattice generated or uncovered by the burn-off. The recovery of sorbates increased the higher the loading of the sorbent (see Table 2). This is due to the limited number of active centres on the surface of the sediment ash. The highest loading corresponds to 800 ppm × 20 components = 1.6 wt% of hydrocarbons on the surface of the sorbent. Even then only traces of 1-naphthol could be detected among the desorption products. Other reactive components, such as dimethylphenol, methylundecanoate and anthracene, were also desorbed incompletely.

To answer the question whether the high activity of the sediment ash is maintained in the presence of native sediment, we carried out thermodesorption runs with 1:1 sediment-

Table 2

Thermodesorption of some hydrocarbons from sediment ash, influence of the sorbate loading (15 s, 400°C), data as recovery rate in %

Component	Sediment loading/ppm			
	100	200	400	800
2,4-Dimethylphenol	<1	9	13	39
Methylundecanoate	<1	3	4	5
n-Pentadecane[a]	100	100	100	100
Phenanthrene	38	60	99	100
Anthracene	11	20	37	61
n-Eicosane	40	53	86	90

[a] This component was chosen as internal standard.

ash mixtures. The mixtures were prepared in several ways. First, a primary sorbent was impregnated as described above, then it was mixed with an equal portion of a clean secondary sorbent. The mixing procedure was carried out by mechanically mixing the solid samples (method A) followed by homogenizing the mixture in a pentane suspension under ultrasonic treatment for 10 min and by evaporating the pentane (method B). The results of the thermodesorption experiments are presented for selected hydrocarbons in Table 3.

Table 3

Thermodesorption of some hydrocarbons from mixed sorbents (contamination 100 ppm of each component, 25 s, 400°C), data as recovery rate in %

Component	Primary + secondary sorbent						
	Sediment	Sediment + sediment ash (method B)	Sediment ash	Sediment ash + sediment (method B)	Sediment ash + sediment (method A)	Sediment ash + water[b]	Quartz powder + DBPO[c]
2,4-Dimethylphenol	43	34	<1	26	16	80	22
Methylundecanoate	13	15	<1	12	10	60	5
n-Pentadecane	100[a]	100[a]	100[a]	100[a]	100[a]	75	90
1-Naphthol	<1	<1	<1	<1	<1	15	<1
Phenanthrene	92	73	35	69	55	100[a]	98
Anthracene	64	53	7	43	31	90	35
n-Eicosane	70	63	38	62	61	60	100[a]

[a] This component was chosen as internal standard.

[b] The sediment ash was impregnated by addition of an acetone–water mixture (3:1, 50 μl per 100 mg ash).

[c] The quartz powder was impregnated with 800 ppm per component of the standard cocktail and additionally with 1 wt% of dibenzoylperoxide.

A special batch of impregnated sorbent used in thermodesorption of sorbent mixtures was subjected to a separate thermodesorption run in order to obtain a more precise picture of mixing effects on the recovery rates. The values obtained for sediment and its ash are close to those presented in Table 1, which refer to other sorbent batches. The data set in Table 3 was condensed to the most conclusive components. It reveals that the high activity of the sediment ash is largely lost in the presence of native sediment. For mixing according to method B it is not important if the sorbate is deposited primarily on the sediment or on the ash. In the case of dry mixing of the impregnated ash with sediment (method A), some remaining activity was observed, but the deactivation was also severe. The data in the next-to-last column of Table 3 give evidence of the reason. There the ash sample was impregnated by adding an acetone–water mixture (3:1, 50 μl per 100 mg sample). Obviously, water is very effective as a desorption agent. Even 1-naphthol was partly thermodesorbed in the presence of water (15% recovery). Since the thermal treatment of sediments is always accompanied by some water release, this could explain the deactivation of the ash in the presence of native sediment.

The last column gives some interesting data reflecting the effects of radicals on thermodesorption yields. For this run, quartz powder was impregnated by adding 1 wt% of dibenzoylperoxide. Its fast decomposition during the thermal treatment generates a high concentration of radicals, which are mainly phenyl and benzoyloxy radicals. Again, those compounds, which were found to interact strongly with sediment and sediment ash, were attacked by the radicals or their decomposition products (e.g. benzoic acid). Phenols and anthracene are known to be very reactive in radical reactions, whereas the high reactivity of methylundecanoate was unexpected. The quite different recovery rates of both the tricyclic aromatics unambiguously reveal the chemical nature of the processes, which cause thermodesorption losses. The chemically more stable phenanthrene was recovered almost completely despite the presence of radicals, whereas its more reactive isomere anthracene was converted to 65%. Because of the similar selectivities of radical reactions and those initiated by different solid sorbents, it is difficult to draw mechanistic conclusions.

Thermodesorption runs with the Py-GC device give conclusive data about the volatile products, but they do not yield information about the residue of the treatment. Therefore, we performed some additional TG experiments (Shimadzu TGA-50, 30 ml min^{-1} He flow, $\dot{T} = 20$ K min^{-1}) with impregnated sediment ash as the target, the results of which is discussed briefly. The sediment itself is not accessible to this approach, because its weight loss is dominated by SOM decomposition. The neat sediment ash was stable in weight up to 550°C. It was impregnated with about 1 wt% of a sorbate component, n-eicosane, anthracene and 1-naphthol, separately. n-Eicosane evaporated completely below 250°C without leaving any carbonaceous residue. Anthracene and 1-naphthol, however, generated significant amounts of residues (about 30% and 70%, respectively) after thermodesorption of the loosely bound portion. These were decomposed only at temperatures above 450°C. The TGA results prove the view that the thermodesorption procedure is accompanied not only by a conversion of one volatile compound into another, but also by their fixation to the sorbent.

Table 4 presents results of pyrolysis experiments in closed glass capillaries. The composition of the sorbate cocktail used was focused on the class of polycyclic aromatics.

ble 4

rolysis of hydrocarbons on sorbents in sealed capillaries at 300°C, data as conversion degrees in %

mponent	b.p./°C	SCR[a]	Quartz powder 16 h	Sediment 16 h	Sediment ash 10 min
Dodecane	216	–	n.d.	<5	<5
phthalene	218	2.33	n.d.	<5	<5
thylnaphthalenes	242	3.33	<5	<5	16
phenyl	254	2.25	<5	<5	0[b]
enaphthene	279	3.33	15	43	>99
lexadecane	287	–	0[b]	0[b]	<5
orene	298	4.00	10	40	93
enanthrene	340	2.60	<5	10	21
thracene	342	3.80	10	40	82
ethylphenanthrene	~350	3.20	<5	15	40
icosane	350	–	<5	<5	5
ethylanthracene	358	5.00	30	29	>99
rene	360	3.50	10	28	87
oranthene	384	3.33	30	30	40
erphenyl	383	2.50	<5	<5	7
rysene	448	3.25	<5	n.d.	40

Structure-count ratio.

Component used as internal standard.

e mixture contained 19 components (14 PAHs, two naphthols and three n-alkanes). e normal charge of sorbates amounted to 500 ppm per component except chrysene 0 ppm). The data are given as % conversion degree. Conversion degrees of less than were considered non-significant. The list of compounds in Table 4 and the following les was reduced to 16 components for reasons of clarity. The naphthols were con- rted completely in all pyrolysis runs, and the methylnaphthalene isomers did not show nificant differences between each other.

It is an important question if the target compounds are in a condensed phase or in the pour phase during the thermal treatment at 300°C in the closed system. Taking them as uids with no interactions with the carrier, as may be true for quartz powder, there is ough gas-phase volume (about 50 mm^3) for complete evaporation even for the highest- iling component chrysene [40]. In the presence of a strong sorbent such as sediment vapour pressure of the target compounds can be estimated only by means of sorption- uilibrium data. However, such isotherms are not available. By extrapolating literature ta [41] and from our own experimental findings discussed below we assume tentatively t at least a significant portion of the PAHs is present in a condensed phase due to par- oning or surface adsorption.

Pyrolysis runs at 300°C with quartz powder as carrier produced low conversion de- es (Table 4, column 4) even after 16 h of pyrolysis. This finding is in line with litera- e data on the thermal stability of PAHs [28,29,38]. It permits the unambiguous attri- ion of higher conversion degrees occurring in the presence of other sorbents to het- geneous reactions or such reactions as are initiated by the sorbent. The presence of a

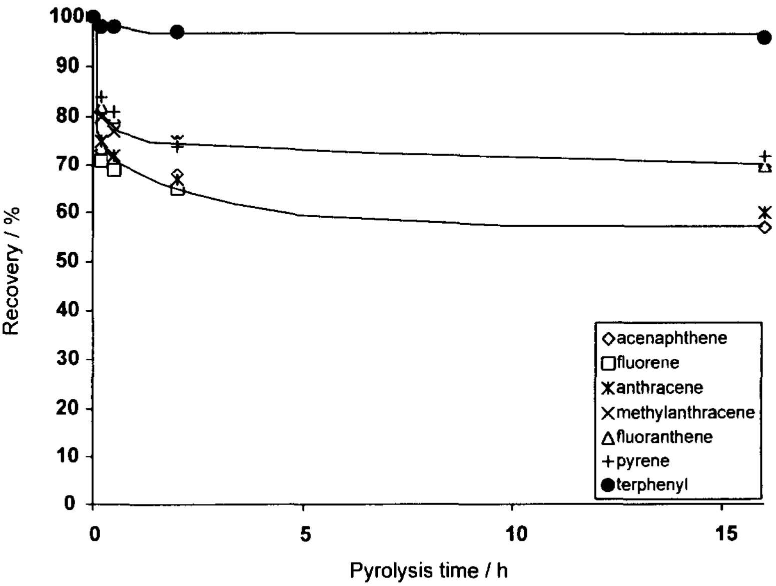

Fig. 3. Pyrolysis of some PAHs at 300°C in a closed reactor with sediment (contamination 500 ppm of 19 components each).

condensed sorbate phase by itself is not sufficient to achieve chemical reactions, as becomes obvious from the time dependence of conversion degrees with sediment (Fig. 3).

Figs. 3 and 4 present recovery rates as a function of pyrolysis time with sediment and

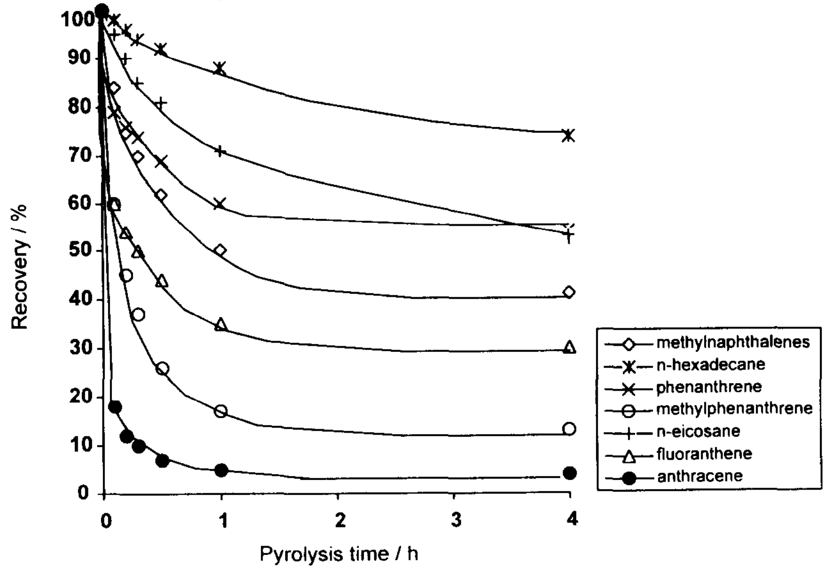

Fig. 4. Pyrolysis of some PAHs at 300°C in a closed reactor with sediment ash (contamination 500 ppm of 19 components each).

iment ash as sorbents. With sediment, the conversion degrees are only slightly higher n with quartz powder after 16 h of pyrolysis (Table 4, columns 4 and 5).

[t becomes obvious from the curves in Fig. 3 that reactions take place mainly at the ;inning of pyrolysis, i.e. during the first minutes. Then, the reaction rates drop steeply. s may be explained by a fast consumption of the thermally reactive groups in the M, which possibly initiate radical reactions. Afterwards, no catalytic effect of the py- /zed sediment on the reactions of the hydrocarbons was observed. Paraffins are not luded in such reactions to any significant extent. From TGA experiments we learned t the weight-loss rate of sediment under isothermal conditions at 300°C is about 0.5% he original SOM content per hour. This value reflects a low reaction rate after passing initial heating-up period.

Sediment ash is much more active, but its activity also drops during the first hour. In- :stingly, some catalytic activity for paraffin cracking remains. The most reactive Hs, acenaphthene, fluorene, anthracene and methylanthracene, are consumed com- :ely after less than 10 min of reaction time. There are great differences in the reactiv- of various PAHs. They are not correlated with the vapour pressure, but with the mical structure of the compounds. The structure/count ratio (SCR) can be taken as a venient reactivity index of PAHs [37,39]. It is defined as the ratio of the numbers of ıcipal resonance structures of a radical formed from a certain PAH and of that PAH lf. It can be calculated from a simple inspection of the molecule's structural formula ,39]. These values for the PAHs studied are collected in column 3 of Table 4. It is ır from Table 4 that PAHs with a SCR value ≥3 are reactive, whereas those having a er SCR are not. This gives strong evidence of the chemical nature of the processes ch control hydrocarbon consumption.

ig. 5 illustrates the influence of the sorbent loading on the hydrocarbon conversion. expected, the recovery of the target compounds rose with an increasing loading of the iment ash. At low loadings (≤100 ppm per component), all compounds, including the reactive ones such as terphenyl, phenanthrene and paraffins, were converted within of reaction time to more than 50%. The most reactive PAHs acenaphthene, methylan- ıcene and fluorene were extensively converted (to 95, 80 and 55%, respectively) even ıe highest sorbent loading, which was about 10 wt% of total hydrocarbons.

No PAHs other than the ones introduced were found by GC analysis in the benzene– :one extracts of pyrolysis residues. Because of the limitation of the GC in analyzing vy components we completed it by some HPLC analyses. No additional PAHs could letected up to chrysene (UV detection at 254 nm). Beyond chrysene, some additional Hs were detected, but not identified. Their concentration, however, was very low. bably, they are intermediates from polymerization of the original PAHs to coke-like :romolecules.

The TG analysis of sediment ash samples, which were previously exposed to PAH py- sis in a closed glass capillary, confirms the results described above for the pyrolysis er flow conditions. The coke-like pyrolysis products started to decompose at tempera- s above 400°C ($\dot{T}$ = 10 K min^{-1}) only. This is a temperature characteristic of thermal ɔmposition instead of evaporation. The combined balance of pyrolysis, extraction and \ comes out even, that means all the PAHs consumed are converted into heavy, 'aromatic, coke-like deposits.

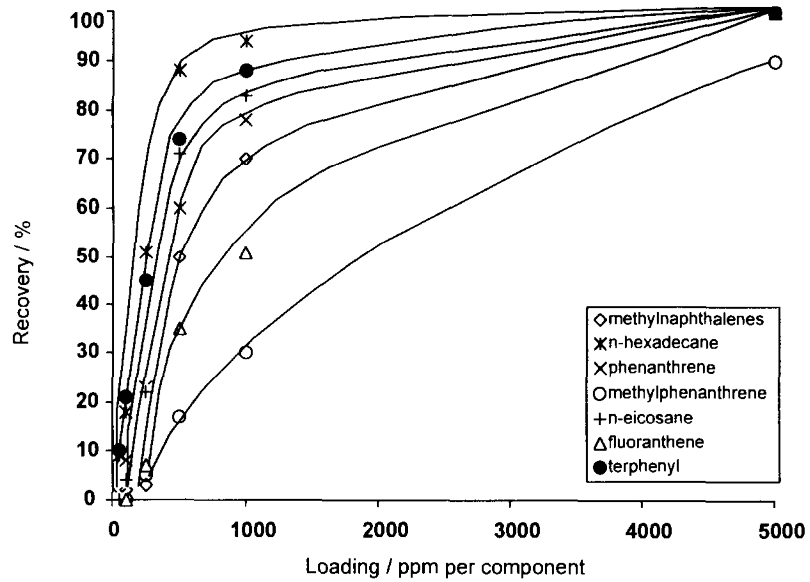

Fig. 5. Pyrolysis of hydrocarbons at 300°C in a closed reactor with sediment ash, dependence of recovery rate on loading of the sorbent (1 h reaction time).

We obtained additional information about the fate of the pyrolyzed PAHs from experiments with two positionally ^{14}C-labelled 9-methylanthracenes (specific activity 20 kBq mg^{-1}), one of them labelled in the methyl group, the other labelled in the central aromatic ring (9 and 10 positions). They were pyrolyzed individually with sediment ash (loading 5000 ppm, 300°C, 1 h). The conversion degree determined by GC analysis was found to be 95%. The gas chromatogram of the extract did not reveal any additional component beside unconverted methylanthracene and anthracene as a trace. This agrees with the balance of radioactivity. Only 5% of the ^{14}C introduced was found in the extract, 93 ± 5% were determined as coke-like deposits on the sediment ash (CO_2 after burn-off). There was no difference between the behaviour of the aromatic and the methyl carbon atoms. This means methylanthracene is polymerized as a whole, without splitting off its methyl substituent.

Table 5 gives degrees of conversion for pyrolysis on various activated sediments. The extreme cases are native sediment with 15.4 wt% of organic matter (OM) and its ash without OM. The other samples were prepared by a thermal or an oxidative pretreatment. There is no simple correlation between the content of OM of the sorbent and its activity. The wet oxidation procedure (H_2O_2/KOH for 1 h under reflux, water washing, drying at 105°C) does not change the activity of the sediment very much. A thermal pretreatment under inert gas flow (300°C for 1 h) causes a lower reduction in the OM content, but the activity of the pyrolysis residue with respect to PAH conversion is increased significantly. This result gives some insight into the nature of the PAH reactions: The prepyrolysis of the sediment eliminates the thermally labile functional groups of the SOM. It is

Table 5

Pyrolysis of hydrocarbons on activated sediments and sorbent mixtures in sealed capillaries (1 h, 300°C), data as conversion degrees in %

Component	Sorbent									
	Sediment untreated	Sediment oxidized with H_2O_2	Sediment 1 h 300°C helium	Sediment 1h 200°C air	Sediment 1 h 300°C air	Sediment 1 h 400°C air	Sediment 1 h 550°C air	Sediment ash + native sediment	Sediment ash + activated sediment (300°C, He)	Sediment ash + activated sediment (300°C, air)
Organic matter content in wt%	15.4	5.0	10.7	12.0	9.2	3.8	0.0	7.7	5.35	4.6
n-Dodecane	<5	<5	<5	<5	<5	6	<5	<5	<5	7
Naphthalene	<5	<5	<5	<5	8	12	12	<5	<5	15
Methylnaphthalenes	<5	<5	<5	10	59	69	50	<5	<5	65
Diphenyl	<5	<5	<5	<5	<5	12	10	<5	<5	15
Acenaphthene	31	58	74	69	>99	>99	>99	54	95	>99
n-Hexadecane	<5	<5	<5	<5	14	29	12	<5	<5	24
Fluorene	33	43	43	47	>99	>99	>99	39	72	>99
Phenanthrene	<5	10	17	8	30	45	42	13	20	36
Anthracene	31	25	32	28	62	95	95	33	35	82
2-Methylphenanthrene	5	13	25	12	82	91	83	19	32	89
n-Eicosane	<5	<5	<5	<5	36	53	29	<5	5	40
9-Methylanthracene	24	38	35	35	>99	>99	>99	43	89	>99
Pyrene	25	16	35	26	62	92	96	31	46	81
Fluoranthene	23	17	30	19	44	64	65	22	31	45
p-Terphenyl	<5	10	24	<5	33	42	34	<5	5	26
Chrysene	n.d.	32	n.d.	32	55	64	69	22	29	61

"thermally stabilized". Despite this, the activity of the sorbent increases. Consequently, PAH consumption is not initiated by the thermal decomposition of the SOM.

A thermooxidative pretreatment enhances the activity of the sorbent more than the corresponding treatment under inert conditions. The most striking feature is the almost equal activity of a sediment after its exposition to air oxidation (300°C for 1 h), which leads to a content of residual OM of 9.2 wt%, and the sediment ash without residual OM. The conversion pattern of both these sorbents is very similar. If the mineral matrix of the sediment, which is uncovered completely and activated in the sediment ash, were the backbone of the sorbent's activity, one should expect a strongly deactivating effect of any residual OM. This is, however, not the case. Either the active centres of the mineral matrix are uncovered by the mild thermooxidative pretreatment, or it generates new active centres, which must be attributed to the residual OM. Whatever the carrier of the activity is, the experimental results demonstrate the linkage between thermodesorption and conversion of PAHs and related compounds during a low-temperature thermooxidative treatment. It should be kept in mind that PAHs belong to the thermally most stable organic compounds. Their oxidized derivatives such as hydroxylated aromatics, which may be formed during hot-air stripping, are even more accessible to heterogeneous chemical reactions. The complete consumption of naphthols during thermodesorption is an example of this behaviour.

The mixing of sediment ash and native sediment (1:1) gives rise to a strong deactivation of the ash down to the low activity level of the sediment. It is the same result as that obtained under flow conditions (see above). The activated sediments have less inhibitory effects. This can be expected from their higher inherent activity levels.

In order to discover the reason for the low activity of sediment ash in the presence of native sediment, we added some protonic compounds (3–15 wt% of water, ethanol and acetic acid) to the impregnated ash. They were assumed to be representative of polar pyrolysis products, which are suspected to cause the deactivation. Although some deactivation was observed, in particular by water, the protonic additives did not affect the ash activity to an extent similar to native sediment. Therefore, we suppose that the heavy, tar-like products from SOM pyrolysis are the reason for deactivation by deposition on, and blockage of, the active centres of the mineral matrix. This view is in conformity with our results concerning the dependence of conversion degrees of PAHs on pyrolysis time and sorbent loading.

4. Conclusions

The results presented in this paper give evidence that the thermodesorption of PAHs and hydroxylated aromatics is accompanied by their chemical conversion to non-volatile products, which can be called charring. The charring of semi-volatile components in low-temperature thermal cleaning processes for the remediation of contaminated soils and sediments can be considered a desirable phenomenon, because it supports the removal of the pollutants even if their volatility is not sufficient for thermodesorption.

Various classes of PAHs were studied. The differences in reactivity observed are in line with known relations between the structure and the reactivity of PAHs in radical reactions. Only polyphenyls, naphthalene and phenanthrene were found to be less reactive. This permits the conclusion that PAHs heavier than those investigated in this study are also reactive with respect to charring. Methyl substituents increase the reactivity of the corresponding aromatic backbone. This is at least true for naphthalene, phenanthrene and anthracene. It clearly points to radical or radical-ion reactions between the sorbed PAHs and active centres of the sorbent.

The sediment ash is much more active in hydrocarbon conversion reactions than the native sediment. This points to the mineral matrix of the sediment as the actual carrier of the catalytic activity rather than the sediment organic matter. Pyrolysis experiments with sediments, which were activated by a thermal and an oxidative pretreatment, support this view. In conclusion, thermodesorption under air flow conditions at temperatures ≤300°C can be considered to be a promising decontamination technique, which may be convenient for in situ application in soils. The air flow stabilizes the catalytic activity of the mineral matrix and may initiate the "thermal humification" of pollutants starting with their partial oxidation. It is worthwhile looking for additives or special conditions which support the charring.

In the present laboratory study only freshly contaminated sediment samples were exposed to a thermal treatment. It may be speculated that "old" pollutants from field samples have penetrated more deeply into the solid matrix [42,43] and, hence, the charring is more pronounced. Further experiments with appropriate sorbents and additives are in progress.

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