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Natural Organohalogens in Sediments

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Abstract. Recent fluvial, lacustrine and marine sediments were found to contain significant concentrations of organohalogens which cannot be explained by known anthropogenic halogen compounds. The assumption of a natural source for the major part of these organohalogens is strongly supported by the fact that in lacustrine sediments deposited some hundred years ago – where no industrial chlorinated organic compounds should be expected – concentrations between 30 and 100 mg/kg of adsorbable organic halogens (AOX, expressed as equivalent chlorine) were detected. In anoxic sapropels of the Black Sea, several thousand years old and having a high organic content (mainly derived from marine phytoplankton), organic bromine and iodine occur at levels up to 313 and 465 mg/kg, respectively.

AOX concentrations in biogenic sediments from various epochs and representing different stages of coalification (peat – lignite – bituminous coal – anthracite) are clear evidence for naturally occurring organohalogens. Plant material has therefore to be considered as the most important *primary* source of high molecular weight organohalogens in sediments. In addition, natural low molecular organohalogens produced by bacteria, fungi, algae (such as haloalkanes, terpenes, amino acids and peptides, chlorophenols etc.) will also accumulate in the sediment and become part of its primary organohalogen content.

As a *secondary* source of organohalogens in sediments their formation in the sediment itself has to be considered. *Biotic* halogenation of organic substrates by haloperoxidases (to occur in algae and other marine organisms but also in terrestrial lichens and fungi) leading to volatile organohalogens has been observed already.

Only little knowledge exists on *abiotic* halogenation. In preliminary investigations in the system trichloroacetic acid – water – humic substances, chlorinated compounds could be identified. A transfer of (low molecular) organohalogens from the sediment into the interstitial water is obvious: If compared with the supernatant lake water, AOX concentrations in interstitial water of Lake Constance sediments are enriched by a factor of 20–70.

Under anaerobic conditions bacterial decomposition of organohalogens leads to the release of halide ions into the interstitial water of the sediment.

The results presented here fully confirm our previous conclusion [1], that the AOX value **cannot** be used exclusively as a sum parameter for **anthropogenic** organic halogen compounds.

1 Introduction: Sediments as Sinks and Sources of Organohalogens

Only recently an overview of the occurrence, biosynthesis, and ecological significance of biogenic chlorine containing organics has been published [2, 3]. The conclusion drawn from the evaluation clearly revealed that the quantity of natural emissions exceeds by far those from industrial production.

The important role of aquatic sediments as sinks and sources of natural organohalogens, and their interactions with interstitial and supernating water, has not been considered in this review. It is therefore our intention to fill the existing gap in this field.

More than two thirds of the earth's surface are covered with water and the bottom of the water bodies is overlain with sediments made up of inorganic and organic particles, transported into the depositional basins from outside, being "allochthonous", and of constituents produced within the basin itself, being "autochthonous".

Sediments can be classified according to their *grain size* and/or to their *composition* and/or to their *mode of*

formation. They are named biogenic, if the predominant constituents have been produced by plants and animals. The content of *"organic carbon"* (as a sum parameter) is a measure of the organic matter in a sediment (or soil), in contrast to *"total carbon"* which comprises organic *and* inorganic carbon.

The most common biogenic sediment with very high concentrations of organic carbon ("carbonaceous") consisting predominantly of macrophytic plant material, grown and deposited in situ, is peat, the initial member of the coalification series with anthracite as the end member. Another biogenic, less common, carbonaceous sediment type is gyttja, composed mainly of relics of plankton grown in the photic zone of eutrophic lakes. If deposited in anoxic water, a sapropelic mud may develop, similar to the sapropel of the Black Sea after the ingression of sea water from the Mediterranean. Organic matter is a minor but very important constituent of all muds with concentrations of a few percent to more than ten per cent of the total solids. Its composition and concentration governs the biological (mainly bacterial) and chemical processes within the sediment after its deposition.

Due to their large surface area and composition (abundant clay minerals and organic matter, both with high ion-exchange capacities) fine-grained sediments ("muds") can adsorb or bind large quantities of inorganic and organic compounds, including persistent anthropogenic pollutants. They are sinks for heavy met-

als, water-insoluble aliphatic and aromatic hydrocarbons, PCBs, and other groups of halogenated hydrocarbons, including DDT and its metabolites, or dioxins and furans [4]. Their water content (now pore- or interstitial water) is very high, but their permeability (in contrast to coarse-grained sediments) extremely low, reducing vertical or lateral mixing within a sediment profile to a minimum. If not disturbed by resuspension or burrowing organisms, soon after deposition, particulate/ interstitial water reactions create a physicochemical-chemical environment, which is governed by the decomposition of the organic matter of the sediment.

In the presence of oxygen a rapid mineralisation of the organic matter leads to CO_2 and H_2O as the main end products. After oxygen depletion – in most recent muds this occurs already in the uppermost millimeters or centimeters – anoxic conditions cause the reduction of sulfate to H_2S by sulfate-reducing bacteria, the generation of ammonia from nitrate, an increase of alkalinity and the formation of methane as a result of a slow degradation of the organic matter [5].

2 Occurrence of Natural Organohalogens in Sediments

2.1 Natural Halogens in Fine-Grained Sediments ("Muds")

In their paper entitled "Halogenorganische Verbindungen in aquatischen Sedimenten: Anthropogen und Biogen" (Organohalogen compounds in aquatic sediments: anthropogenic and biogenic). MÜLLER & SCHMITZ [1] published results demonstrating considerable concentrations of organohalogens in recent marine, fluviatile and lacustrine fine-grained sediments (69–245 mg/ kg, expressed as equivalent chlorine) and in sewage sludge (205–340 mg/kg), which by far could not be explained by the sum of anthropogenic chlorinated hydrocarbons (PCBs, pesticides, chlorobenzenes, etc.) that only accounted for a few per cent or less of the "Total Organic Halogens", TOX, of the sediments. A non-anthropogenic, natural biogenic source for the bulk of the sedimentary TOX was therefore assumed. This assumption was strongly supported by the fact that, in "older sediments" of Lake Constance, deposited already in the last century, no traces of industrial chlorinated hydrocarbons – as to be expected – but still high TOX concentrations were found. Another indication of a non-anthropogenic origin of sedimentary organohalogens was the predominance of *bromine* in marine sedimentary organohalogens whereas in non-marine sediments *chlorine* prevailed.

A similar discrepancy between (defined) anthropogenic organohalogens and the sum of TOX had been observed already earlier in river water [6]. MÜLLER
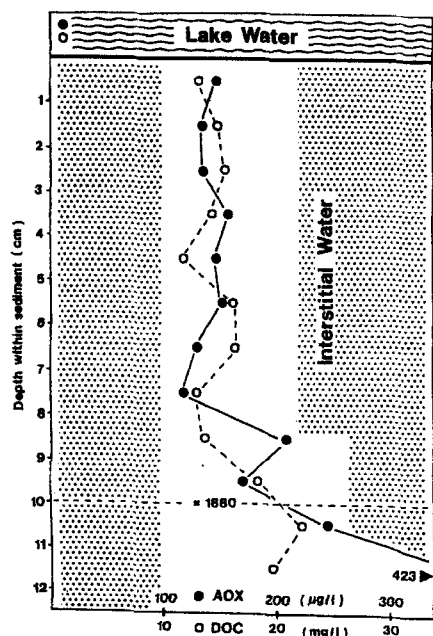

Fig. 1 AOX and DOC in interstitial water of Lake Constance sediments as compared with Lake supernatant water after Schmitz et al., 1986

& SCHMITZ [1] therefore postulated: "Exchange reactions between sediment and supernatant water (via interstitial water) might lead to a release of natural organic halogen compounds accumulated, transformed or newly formed within the sediment, which then contribute to the 50–90% of still unknown halogen compounds that make up the TOX in water analyses". One year later, SCHMITZ et al. [7] could verify exchange reactions leading to a release of "Adsorbable Organic Halogens" (AOX) from the sediment into the interstitial water with results obtained in sediment cores from Lake Constance. The concentrations of AOX and dissolved organic carbon (DOC) in the interstitial water of a sediment core collected in the central part of the lake at a water depth of 140 m are depicted in Fig. 1. If compared with the

Table 1 AOX and C_{org} in sediment core samples from Lake Mindelsee (Germany)

	Depth (cm)	AOX (mg Cl/kg dw.)	C_{org} (%)
1	0-2	50.6	3.43
2	2-4	60.6	3.41
3	4-6	40.2	3.32
4	6-8	66.6	3.29
5	8-10	92.8	2.83
6	10-12	42.6	–
7	15-17	50.0	2.59
8	20-22	58.0	2.25
9	25-27 (>200 years)	36.5	2.34
10	30-32	34.0	2.68

supernatant lake water (6 ± 1 µg/l AOX; 1.1 ± 0.05 mg/l DOC) AOX concentrations lie in the range between 119 and 423 µg/l, which means that they are enriched by a factor of 20.0–70.5. By analogy with other dated sediment cores from this part of the lake, it can be assumed that the sediment layers below 10 cm – with the highest AOX concentrations in the interstitial water! – were deposited already before 1880 [8]. An anthropogenic origin of the organohalogens is therefore most improbable.

Sediments of a 32 cm long core from the Mindelsee, a small lake in a protected national reserve near Radolfzell, SW-Germany, representing a time interval of the last 300 years, contain 34.0–92.8 mg/kg Cl and 2.25 –3.43% C_{org}, respectively (Table 1). No systematic change with depth (age!) could be observed.

Of eminent importance are geochemical data from Black Sea sediment cores collected by the ATLANTIS II in 1969 [9]. Fig. 2 shows the concentration of organic carbon and bromine in the sediment core No. 1432 from the central basin. The lower unit (101–63 cm) of the core represents the characteristic Black Sea sapropel which was formed during the beginning of the anoxic

stage of the basin when the connection with the Mediterranean was re-established about 6 600 years ago. The youngest unit (uppermost 25 cm) represents the sediments formed during the past 1 600 years when the salinity in the basin reached the present value and coccoliths were introduced from the Mediterranean. The two units are separated by a mud-flow or turbidite layer.
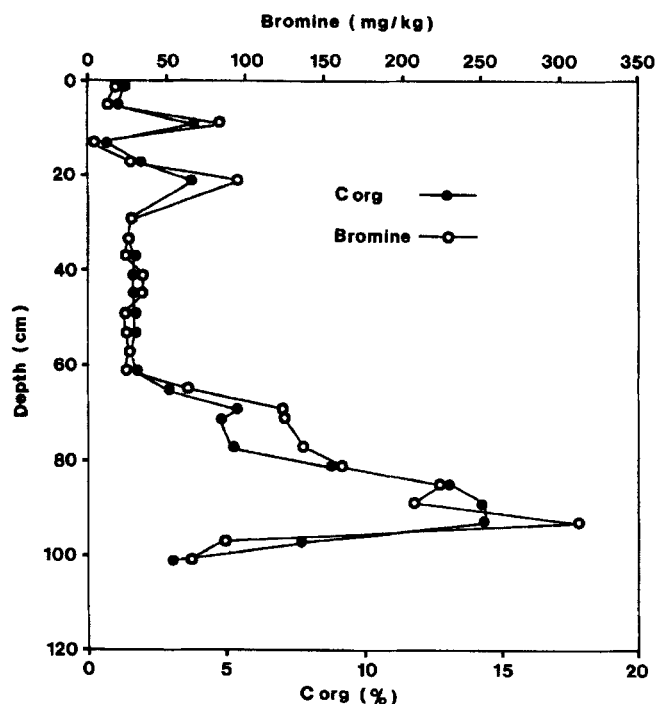

Fig. 2 Concentrations of organic carbon and bromine in a sediment core of the Black Sea after Calvert, 1990

The bromine concentrations range between 3 mg/kg (C_{org} 0.66%) and 312 mg/kg (C_{org} 14.39%); they are highest in the sapropel, intermediate in the youngest unit and lowest in the mud-flow layer. A highly significant positive correlation exists between Br and C_{org}. The C_{org}/Br×1000 atomic ratio is very constant, varying only between 2.5 and 5.9. Iodine concentrations vary between 4 and 467 mg/kg but no correlation exists between iodine and C_{org} in the sapropel unit.

2.2 Natural Organohalogens in Plants and Carbonaceous Sediments

2.2.1 Natural Organohalogens in Macrophytes

Marine plants have long been known for their organically bound chlorine, bromine and iodine [10, 11] and their capacity to produce organohalogens. In the meantime, more than a thousand defined natural low to intermediate molecular weight chlorine- and bromine-containing compounds, extractable in organic solvents,

have been identified as metabolites in different aquatic – both marine and freshwater – macrophytes, algae and terrestrial plants and – to a much lesser extent – from animals [12, 13]. These metabolites are in some cases of pharmacological importance or are thought to be biochemical regulators playing a defensive role in the biota concerned [14, 15, 16, 17, 18]. Only recently MANÖ & ANDREAE [19] described the emission of methyl bromide from biomass burning, which indicates that bromine might play a more important role also in terrestrial plants. Already in 1989 VUYNOVICH [20] explained bromide concentrations in the interstitial water of sediments of Lake Constance, increasing from the top to the deeper parts of the sediment column, as dehalogenation products of sedimentary organic matter. In continuation of these studies on interstitial water in anoxic sediments, SONG & MÜLLER [21] came to the same conclusion (see chapt. 4) for sediments of the Neckar river.

Experiments with organic solvents resulted in a very low extractability of halogens determined as TOX or AOX of the sediments. The conclusion drawn in our 1985 publication, that high molecular weight biogenic organohalogens, insoluble in organic solvents, must be responsible for the bulk of the AOX content, is still valid. It can be assumed that these compounds are an integral part of cellular macromolecules [22].

As we regarded plants as the major source of natural organohalogens in sediments, AOX concentrations were determined in various plants [23].

Five macrophyte genera grown in a protected greenhouse (in soil not contaminated with chlorinated pesticides) in the Botanical Garden of the University of Heidelberg revealed AOX concentrations between 65 and

115 mg/kg Cl. AOX contents of selected aquatic plants grown in the intertidal or supratidal zone of the North Sea were only slightly higher.

To exclude a possible "contamination" by inorganic halides, an argument often used by opponents of the "natural organohalogen theory", we developed methods to remove halides prior to AOX analysis [24]. We experimented with ultra-sonication, shock-freezing and ultra-turax treatment and combinations thereof. Repeated shock-freezing (in liquid nitrogen) and thawing of the ultra-turax crushed plant material led to a complete destruction of the cells into cell-wall fragments and to the release of the ionic halogen species already after two cycles. To be on the safe side in routine analysis we recommend four shock-freezing/thawing cycles. Fig. 3 depicts the AOX concentrations found in leaves of *Vinca major* after a series of cycles.

2.2.2 Natural organohalogens in carbonaceous sediments (peat – lignite – coal)

Different species of *Sphagnum*, important mosses in recent peat formation and major constituents of Holocene ombrotrophic peat, exhibited AOX concentrations between 70 and 90 mg/kg [25]. Table 2 contains the concentrations of AOX and C_{org} in a peat profile from the Erzgebirge (Saxony, Germany) with an age between 2 500 and 3 000 years for the lowermost part of the profile. C_{org} concentrations are relatively constant (47.1
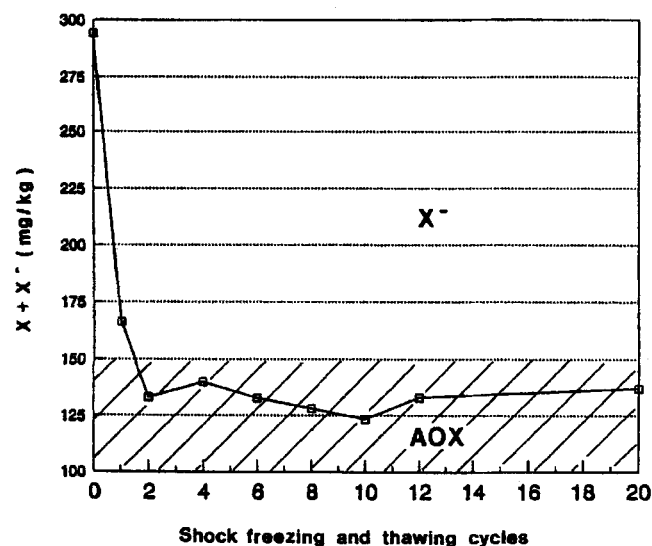

Fig. 3 Removal of inorganic halides by repeated shock freezing and thawing (crushed leaves of *Vinca major*)

Table 2 AOX-concentrations in a peat profile from the Erzgebirge (Saxony – Germany)

	Depth (cm)	AOX (mg Cl/kg)	C_{org} (%)	Dating (yr±d)[a]
1	0-10	229.5	47.1	
2	10-20	397.8	56.4	
3	20-30	239.4	53.4	1260±70
4	30-40	169.7	59.4	
5	40-50	262.4	49.5	1410±70
6	50-60	201.3	51.0	
7	60-70	183.4	48.9	1930±110
8	70-80	153.2	47.9	
9	80-90	132.0	49.1	1940±70
10	90-100	135.1	46.9	
11	100-110	122.4	48.6	1970±80
12	110-120	133.0	49.1	
13	120-130	175.2	47.3	2050±70
14	130-140	184.6	46.9	
15	140-150	190.7	48.8	
16	150-160	230.1	51.0	2290±70
17	160-170	253.8	50.4	
18	170-180	342.8	54.7	2500±80
19	180-200	269.6	56.8	

[a] Data after BOZAU, 1995

-59.4%) whereas the AOX contents vary between 122.4 and 397.8 mg/kg. Lower concentrations (< 200 mg/kg) cluster in the middle of the profile, higher concentrations are found in both the lower and higher sections. If compared with recent *Sphagnum* AOX, concentrations in peat are generally higher.

First AOX determinations in coals with different rank of coalification gave the following results:

Lignites, Tertiary, Germany, 107 and 166 mg/kg, respectively.

Bituminous coal, Carboniferous, England, 74 mg/kg.

Anthracite, Carboniferous, Pennsylvania, USA, 54 mg/kg.

Earlier studies on British coals [26] and on Illinois coals [27] revealed appreciable amounts of excess chlorine, relative to stoichiometric NaCl (or other chlorides such as KCl). The conclusion drawn by GLUSKOTER & RUCH [27] (p. 65): "The chlorine present in a form other than sodium chloride is most likely in organic combination" is just another way to allude to "organochlorine".

## 3 Origin of Natural Organohalogens in Sediments

3.1 Primary Sources

As demonstrated in the previous chapter, plants – both marine and terrestrial – have to be considered as the most important primary sources of high molecular weight organohalogens in sediments, which are insoluble in organic solvents. *Sphagnum* mosses are an excellent example for terrestrial macrophytes containing primary organohalogens which – due to their stability – are enriched during biogeochemical processes leading to peat and can even persist during the transformation to lignite and coal. The Holocene Black Sea sapropel, on the other hand, contains very high natural organobromine concentrations bound to the organic matter derived from marine phytoplankton. In addition, natural organohalogens *produced* by bacteria, fungi, marine algae – low molecular compounds extractable in organic solvents, such as haloalkanes, terpenes, amino acids and peptides, chlorophenols etc. (for compilation see GRIBBLE [13, 28, 29]) – will also accumulate in the sediment and become part of its primary organohalogen content. They will fall into the group of Extractable Organic Halogens (EOX) or even Purgeable Organic Halogens (POX) which clearly distinguish them from the high molecular weight organohalogens measured by AOX analysis.

3.2 Secondary Sources

The very high AOX (and DOC) concentrations in the sediment interstitial water (if compared with the supernatant lake water) of Lake Constance (Fig. 1) can be interpreted as reaction products of processes which started immediately after the deposition of a sediment layer. The question, whether these products are fragments of primary high molecular weight organohalogens and/or de-novo structures synthesized within the sediment, needs to be clarified. Two main processes should be considered for a de-novo formation:

3.2.1 Biotic Halogenation of Organic Matter

Haloperoxidases are enzymes which can catalyze the oxidation of halides in the presence of hydrogen peroxide, resulting in a halogenation of organic substrates [15, 30] according to the following equation:

$$\text{Substrate-H} + H_2O_2 + X^- \xrightarrow{\text{haloperoxidase}} \text{Substrate-X} + H_2O$$
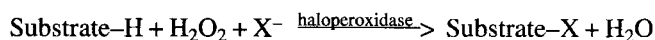
Haloperoxidases have been isolated from various classes of marine algae and other marine organisms [31, 32] but have also been found in terrestrial lichens, fungi, horseradish roots, in milk and in soil extracts [33, 34]. Hydrogen peroxide may be formed through incomplete reduction of oxygen in the respiration process or during photosynthetic water oxidation [3].

It can be assumed that exoenzymatic halogenation takes place only in the oxic layers of sediments, since peroxides are essential to initiate the biotic halogenation.

3.2.2 Abiotic Halogenation of Organic Matter

Only little knowledge exists on abiotic non-enzymatically catalyzed reactions leading to organohalogens. Current studies are focused on trichloroacetic acid (TCA) as a chlorinating agent. TCA has been monitored in natural samples (non-contaminated soil, humic substances, glacier, peaty water), and trace amounts of TCA were also detected by the reaction of acids from the citric acid cycles with haloperoxidase. In preliminary investigations in the system TCA – water – humic substances, chlorinated compounds could be identified, giving evidence for an abiotic halogenation of organic matter [35, 36].

4 Dehalogenation Processes in Sediments

In his dissertation on interstitial water of Lake Constance sediments VUYNOVICH [20] found that bromide concentrations were "not detectable" (< 0.001 mg/l) at the water/sediment interface and gradually increased with increasing depth in the sediment to 0.25 mg/l Br$^-$ in the deepest horizon at 77 cm. Similar ob-
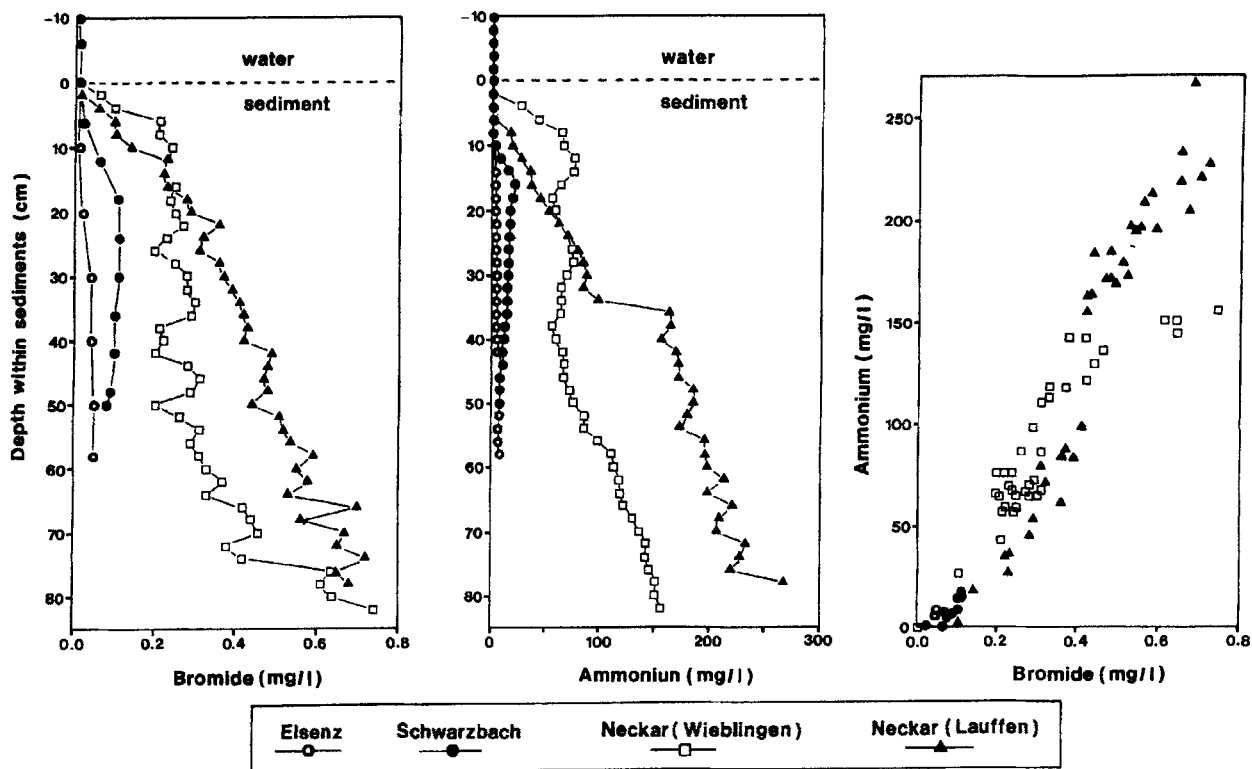
Fig. 4 Bromide, ammonium and bromide : ammonium correlation in interstitial water of Neckar sediments after Song & Müller, 1993

servations were made in interstitial waters of sediments of the Neckar river [21]: With increasing depth in the sediment, bromide concentrations increased from 0.02 mg/l (water/sediment interface) to a maximum of 0.74 mg/l in the deepest section of the "Wieblingen" sediment core (Fig. 4). A parallel tendency was observed with ammonium concentrations and alkalinity (not depicted in Fig. 4). The correlation alkalinity : ammonium reflects the mineralization of organic matter in anoxic environments by denitrification, iron and manganese reduction, sulfate reduction and methane production. The very high correlation between bromide : ammonium and bromide : alkalinity leads to the conclusion that bromine, originally a constituent of the organic matter of the sediments, is released as bromide during an early anaerobic stage of diagenesis.

The relatively high concentrations of chloride in river and lake water (and correspondingly also in the interstitial water of the sediments) make it practically impossible to trace the release of minor chloride concentrations from organic matter into the interstitial water. So even in freshwater environment, bromine is an excellent fingerprint to study processes of dehalogenation. Concentrations of water-insoluble bromine (AOX) in a sediment core of the Neckar river collected at Lauffen varied between 43 and 95 mg/kg Br, leading to the conclusion that also in terrestrial plants bromine might play

a significant role in halogen biochemistry. The interstitial water investigations reveal that aquatic sediments act both as sinks and sources in the biogeospheric cycling of bromine which, after its release from the organic matter of the sediments into the interstitial water, will finally reach the river or lake by diffusion and/or compaction pressure.

5 Conclusions

Fine grained sediments ("muds") containing organic matter and "carbonaceous" sediments (e.g. peat) are important sinks and sources of natural organohalogens which – even in the worst case of anthropogenic contamination – make up the bulk of sediment AOX. High molecular weight organohalogens (with bromine prevailing in marine environments and chlorine in freshwater systems) are primary plant constituents. After deposition as "organic matter", in the presence or absence of oxygen at the sediment/water interface – and later within the sediment itself – determines the fate of natural organohalogens. Under *anoxic* conditions they undergo alterations leading to a dehalogenation connected with the transfer of halide ions into the interstitial water of the sediments.

Under *oxic* conditions, low molecular weight orga-

nohalogens may be formed by *biotic* halogenation in the presence of haloperoxidases. Only little is known on *abiotic* non-enzymatically catalyzed reactions. There is some evidence that trichloroacetic acid might react with humic substances to form chlorinated compounds.

The question whether (natural) AOX in the interstitial water of sediments are fragments of primary high molecular organohalogens or/and de-novo structures synthesized within the sediment, needs to be clarified. Further investigations are required to solve a series of important questions, such as (to name just a few):
- nature and structure of high molecular weight organo halogens
- differentiation and determination of halogens (Cl, Br, I, F) in various matrices
- experimental bioaccumulation of halogens in tank experiments with green algae (e.g. *Scenedesmus*)
- synchronous field investigations of *both* sediment and interstitial water
- ion-selective in situ measurements of important interstitial water parameters over a longer period of time
- alteration of organohalogens in different stages of coalification

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