Bull. Environ. Contam. Toxicol. (1997) 58:961-968

Bulletin of Environmental Contamination and Toxicology

Influence of Storage on Sediment Characteristics and of Drying Sediment on Sorption Coefficients of Organic Contaminants

R. T. H. M. Sijm,[1] M. Haller,[1] S. M. Schrap[2]

[1]Environmental Chemistry Group, Research Institute of Toxicology, P.O. Box 80.058, NL-3508 TB Utrecht, The Netherlands
[2]Institute for Inland Water Management and Waste Water Treatment, RIZA, P.0 Box 17, NL-8200 AA Lelystad, The Netherlands

Received: 28 October 1996/Accepted: 10 February 1997

Organic contaminants are released in the environment and are distributed over water, sediment, air, soil, and biota. To describe and predict the distribution of organic chemicals between water and sediment, sorption coefficients are being used. Sorption is usually regarded as a simple partitioning process between water and sediment. The sorption coefficient K_p (L/kg) is defined as the ratio of the concentration of a compound in sediment (C_s, mg/kg) and in water (C_w, mg/L) at equilibrium (Chiou et al. 1979; Karickhoff et al. 1979; Karickhoff 1980; Chiou et al. 1983): $K_p = C_s/C_w$.

Since sorption coefficients and organic carbon content of sediments vary significantly (Schrap and Opperhuizen 1989), and the organic carbon of sediment has been identified as being responsible for a significant part of the sorption capacity of the sediment for organic contaminants, it has been proposed to normalise different sediments for their organic carbon content (Karickhoff et al. 1979. Although the value of the organic carbon normalisation has been discussed (Gauthier et al. 1987; Schrap and Opperhuizen 1989; Capel and Eisenreich 1990; Grathwohl 1990; Rutherford et al. 1992; Xing et al. 1994), the importance of the organic matter of sediment has been generally recognized. However, storage and pretreatment, i.e. drying, of the sediment may change this organic carbon content and/or composition (Sverdrup et al. 1990). Sediment may be dried at higher temperature to remove unwanted contaminants, before it is used in experiments. This 'background' contamination makes the direct usage of the sediments to determine sorption coeflicients of (other) organic contaminants difficult since these contaminants may disturb analytical detection, such as e.g. GC-ECD for chlorinated organic compounds.

The aim of the present study was to investigate the influence of storage on the fraction organic carbon and other sediment characteristics (inorganic carbon content, dry weight, nitrogen content, phosphorus content, iron content, manganese content, and the fraction of particles <200 mm), and of drying the sediments on sorption coefficients of a series of chlorinated benzenes and nitrobenzenes.

MATERIALS AND METHODS

1,2,3-Trichlorobenzene (123CBz, Aldrich), 1,2,3,4-tetrachlorobenzene (1234CBz, Aldrich), pentachlorobenzene (pentaCBz, Riedel-de-Häen), 2,3,5,6-tetrachloronitrobenzene (2356CN, EGA-Chemie), 2,3,4,5-tetrachloronitrobenzene

---

Correspondence to: R.T.H.M. Sijm

(2345CN, EGA-Chemie) and pentachloronitrobenzene (pentaCN, Aldrich) were used as test chemicals for the sorption studies. *n*-Hexane (Janssen) was redistilled prior to use as organic solvent.Florisil (60-80 mesh) was obtained from Merck. Sediments were sampled from different locations in The Netherlands: Oostvaardersplassen (OVP), Ketelmeer (KM), Noordzeekanaal (NZK), and Ransdorperdie (RDD). Organic carbon of NZK and RDD sediments were 1.68% and 20.6%, respectively. For organic carbon of OVP and KM sediments see Table 3. After sampling, the wet sediments were stored in a closed bucket at 5°C. The OVP sediment was wet sieved through a 1 mm sieve before storage. Organic carbon content, inorganic carbon content, dry weight, nitrogen content, phosphorus content, iron content, manganese content, and the fraction of particles <200 mm of wet OVP sediment were determined after 1, 2, 4, 6, 15, 32, 66 and 94 months. In addition, the organic and inorganic carbon contents of wet and dried KM (200°C) and OVP (200°C and 300°C; after 15, 66 and 94 months of storage, respectively) sediments were determined. For the other sediments, only the organic carbon percentages of the wet sediments were determined.

Sediment characteristics were determined following in-house available methods, which will shortly be described below. The total inorganic and organic carbon content was determined following CO_2-evolution after catalytic burning of the sediment. The organic carbon content was determined with sediment which had been treated first with hydrochloric acid. The inorganic carbon content was determined as the difference between the total organic carbon content and the organic carbon content. CO_2 was analyzed by gas chromatography. Sediment was freeze-dried for one week and dry weight was determined gravimetrically. A portion of the sediment was destructed using concentrated sulphuric acid and potassium sulphate and mercury (II) oxide as catalysts and total phosphorous content and total Kjeldahl nitrogen content were determined photometrically using a flow-through system. Fe and Mn contents were determined using atomic emission spectrometry (ICP-AES). The fraction of particles smaller than 200 µm was measured gravimetrically.

Table 1. Conditions of drying the sediment

	wet	160°C 24h	160°C 5d	200°C 24h	200°C 5d	300°C 24h
NZK	x[a]	x	x	x	x	x[a]
RDD	x[a]	x		x		x[a]
OVP	x[a]	x		x		x[a]
KM	x[a]			x		

x measurement; [a] determination of sorption coefficients

After drying, 1 g of sediment was homogenized in a mortar and refluxed under heating for 90 minutes with 50 mL of distilled water and 50 mL of hexane as described by Schrap et al. (1994) to determine remaining ‘background’ contamination using gas chromatography. A batch shake method was used to determine sorption coefficients in triplicate of the series of chlorinated benzenes and nitrobenzenes in wet and dried (300°C) OVP, RDD and NZK sediments, according to Schrap et al. (1994). In summary, 1 g/L of sediment was shaken during 48 hours at 20°C with the test compounds (123CBz: 436.5 µg/L; 1234CBz: 598.3 µg/L; pentaCBz: 179.2 µg/L; 2345CN: 545.6 µg/L; 2356CN: 764.6 µg/L; pentaCN:

238.6 µg/L), which had been dissolved in water using a generator column method (Opperhuizen 1986). Then, the sediment suspension was centrifuged at 900g for 20 minutes. Sediment and water were separated and refluxed under heating for 90 minutes with 50 mL of distilled water and 50 mL of hexane. For cleanup of the concentrated hexane extracts, florisil that was deactivated with water (2 mL per 10 g) was used. One portion of NZK sediment which had been refluxed under heating was used to study the influence of hexane pretreatment of the sediment on the sorption coefficients of the series of test compounds.

To compare the sorption coefficients from the different experiments and sediments, the relative sorption coefficient (R_{ij}) for two compounds *i* and *j* are determined as follows: $R_{ij} = K_{p,i}/K_{p,j}$, in which $K_{p,i}$ and $K_{p,j}$ are the sorption coefficients of compounds *i* and *j*, respectively.

A Hewlett Packard gas chromatograph 8580A equipped with a ^{63}Ni electron capture detector was used. Injection (1tot 2 µl) was splitless at 250°C. A 15 m DB-5 capillary column (J&W Scientific) was used with an internal diameter of 0.32 mm, and a film thickness of 0.25 mm. Carrier gas was 1-2 mL/min helium, and make-up gas was 60 mL/min Ar/CH_4 (90:10). Detector temperature was 325°C.

RESULTS AND DISCUSSION

Most of the OVP sediment characteristics (i.e., d.w., N, P_{tot} Fe, Mn, and the fraction of particles <200 mm), do not significantly change during storage (Table 2). The most striking influence of wet storage is that the organic carbon content of OVP sediment significantly decreases from 3.79% to approximately 2.7% during the first 6 months. Prolonged storage until 94 months dots not result in a further decrease of the organic carbon (Table 2). In spite of the low storage temperature (5°C), degradation of the organic carbon thus seems to have taken place. Since sorption coefficients are usually normalized by f_{oc},the resulting K_{oc} of a test compound in a given sediment will thus differ significantly after prolonged storage time, when the changing organic carbon content has not been appropriately adjusted to the time when the sorption coefficients have been determined.

The hexane extracted wet sediments show many peaks after gas chromatography analysis, indicating the presence of many contaminants and/or disturbing agents in the natural sediments. In particularly, NZK sediment contained many disturbing signals at GC-ECD analysis. Drying conditions diminished the ‘background’ contamination by reducing the number and extent of peaks in the GC-ECD chromatograms of the sediments (not shown). It was observed that drying at a high temperature during 24 h removes the 'background' contamination more effectively than drying for 5 d at a lower temperature. Drying is thus very useful in cleaning up the sediments for sorption experiments purposes.

The organic carbon content of both OVP and KM sediments decreased after drying for 24 h at 200°C, while the inorganic content of OVP sediment was not affected (Table 3). KM sediment thus lost approximately 30% of its organic carbon by drying at 200°C, while the decrease in organic carbon for OVP varied between 4 and 50% (Table 3). Drying the sediment at 300°C decreased the organic carbon fraction dramatically to 0.07% (Table 3). Also the study of Banwart et al. (1980) showed a 3-20% decrease of the organic carbon content of two sediments which were ovendried at 110°C for 48 h. Depending on drying temperature and on sediment a different decrease in organic carbon content is thus observed

Table 2. Sediment characteristics of wet OVP sediment during storage at 5°C in a closed bucket.

months after sampling	o.c.[1] %	i.c.[22] %	d.w.’ %	N[4] g/kg	P_{tot}[5] g/kg	Fe[6] g/kg	Mn[7] g/kg	< 200 mm[8] %
0	3.79	1.27	-	-	-	-	-	-
1	3.16	1.47	-	-	-	-	-	-
2	2.78	1.25	40.3	-	-	22.9	1.11	69
4	2.92	1.46	39.6	3.1	0.8	22.9	1.03	72
6	2.74	1.39	38.0	4.1	0.54	22.6	1.09	53
15	2.52	1.65	40.0	2.7	0.63	-	-	53
32	2.49	-	-	-	-	-	-	-
66	2.75	0.8	36.3	3.72	0.67	-	-	-
94	2.70	-	-	-	-	-	-	-

- not measured; [1]organic carbon content; [2]inorganic carbon content; [3]dry weight; [4](oxidised Kjeldahl) nitrogen content: [5]total phosphorous content; [6]iron content; [7]manganese content; [8]fraction of the sediment particles smaller than 200 mm; all data are given on a dry weight basis, except for dry weight itself which is a percentage of the wet weight of the sediment.

Table 3. Organic (o.c.) and inorganic (i.c.) carbon percentages of wet sediment and the influence of drying of OVP and KM sediment.

sediment		o.c.[1] %	i.c.[2] %
OVP (15 months)	wet	2.52	1.65
	dried (200°C, 24 h)	2.38	1.56
OvP(66months)	wet	2.75	0.8
	dried (200°C, 24 h)	1.33	-
OVP (94 months)	wet	2.70	-
	dried (300°C, 24 h)	0.07	-
KM	wet	3.34	-
	dried (200°C, 24 h)	2.07	-

- not measured

The sorption coefficients of the chlorinated benzenes and nitrobenzenes are significantly higher in the wet than in the dried (at 300°C) OVP, RDD and NZK sediments (Table 4). Sorption coefficients of the test compounds in wet OVP sediment are a factor 2.8 to 7.5 higher than those in dried sediment, while for RDD and NZK sediments these factors are

4.4 to 8.4 and 12. I to 14.4, respectively. Sorption coefficients in dried NZK sediment were very low for most of the test compounds. Only for pentaCBz and pentaCN sorption coefficients could be determined in dried NZK sediment (Table 4). No significant differences were found between sorption coefficients in wet and hexane pretreated NZK sediment (Table 4).

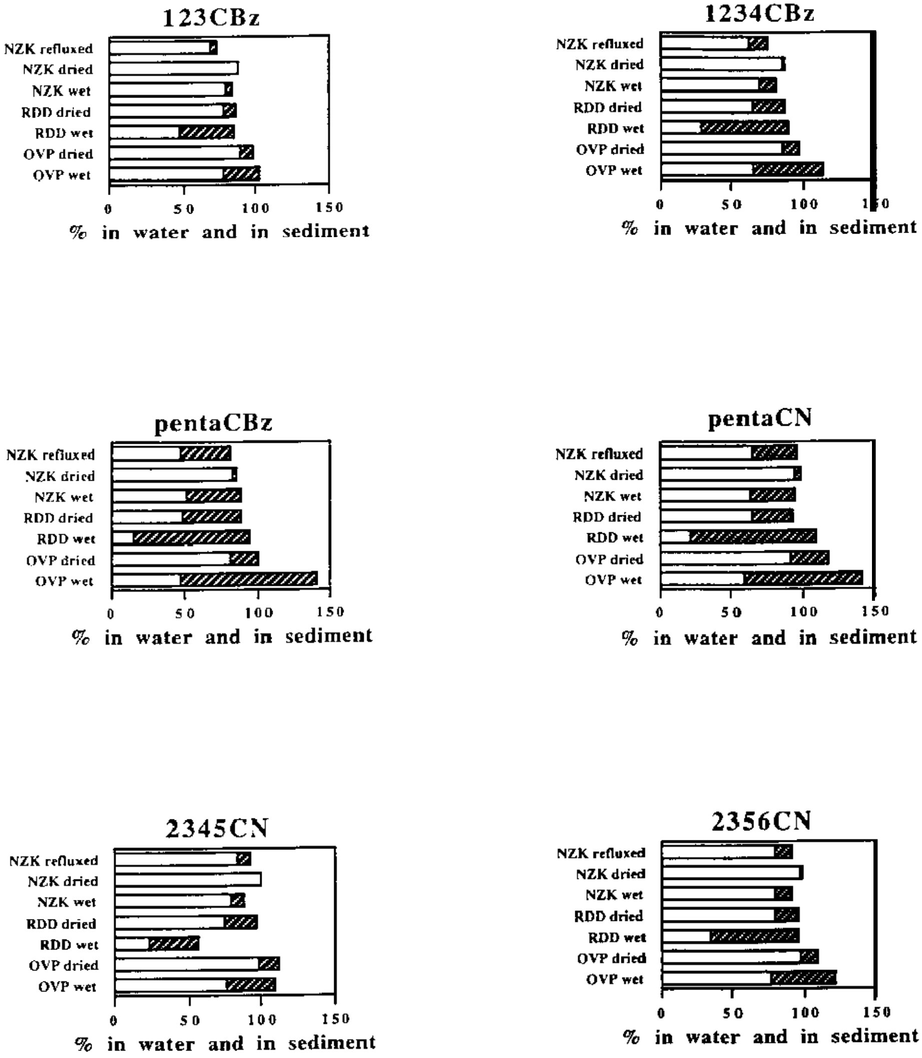

Figure 1. Mass balances of the sorption studies of the chlorinated benzenes and nitrobenzenes in wet and dried OVP, RDD and NZK sediment, and in hexane pretreated NZK sediment (NZK refluxed). The amount of test compound which had been added to the sediment in water has been set to 100%.

The differences of the sorption coefficients between wet and dried sediments can partly be explained by the influence of ‘background’ contaminants which may have added to the administered amounts of the test compounds in the sediment. The mass balances (means of triplicates, Figure 1) show that in some cases up to 140% of the added amounts of e.g. pentaCN and pentaCBz were found in OVP sediment at the end of the study. This indicated that there may have been some of these compounds already present in the sediment before addition of the contaminated water, which is corroborated by the ‘background’ contamination.

A second explanation for the lower sorption coefficients of the dried sediment is that drying may have removed a large part of the organic carbon essential for sorption. Table 3 shows that the organic carbon content after drying at 300°C has decreased dramatically for the OVP sediment. However, these differences are not in parallel with the decrease in organic carbon percentage of the sediments after drying, as the results for OVP sediment show. The sorption coefficients decrease with a factor 2.8-7.5 only, while the organic carbon content decreases almost a factor 40. It must be realised that heating the sediment will not only decrease the organic carbon content, but will also affect the composition of the organic carbon, which may be changed or destructed. The latter, however, cannot be observed by measuring the organic carbon percentage, while it may have a significant influence on the sorption capacity of the organic carbon.

Table 4. Average (± SD) sorption coefficients of the chlorinated benzenes and chlorinated nitrobenzenes with dried (300°C) and wet OVP, RDD and NZK sediments, and with hexane (refluxed) pretreated NZK sediment (n=3).

	123CBz	1234CBz	pentaCBz	2345CN	2356CN	pentaCN
OVP						
wet	293 (20)	720 (50)	1960 (80)	421 (40)	540 (30)	1330 (50)
dried[a]	100 (-)	150 (-)	260 (-)	150 (-)	130 (-)	220 (-)
wet÷dried	2.9	4.8	7.5	2.8	4.2	6.0
RDD						
wet	710 (50)	2050 (160)	5100 (400)	1280 (130)	1640 (130)	3940 270)
dried	120 (50)	360 (50)	860 (50)	290 (60)	230 (60)	470 (60)
wet÷dried	5.9	5.7	5.9	4.4	7.1	8.4
NZK						
wet	70 (60)	200 (50)	720 (80)	100 (40)	160 (40)	510 (70)
dried	-	-	50 (40)	-	-	42 (22)
refluxed	70 (0.3)	218 (5)	720 (20)	95 (4)	158 (2)	470 (20)
wet÷dried	-	-	14.4	-	-	12.1
wet÷refluxed	1.0	0.92	1.0	1.1	1.0	1.1

[a]n=2; - could not be determined

Sorption coefficients are lower in the dried sediments than in the wet sediments (Table 4). The sorption coefficients, however, in wet and in dried sediments increase with increasing chlorine content of both the chlorinated benzenes and the chlorinated nitrobenzenes, i.e.

the K_p of e.g. pentaCBz is always higher than the K_p of 1234CBz, in all sediments (Table 4). Relative sorption coefficients (R_{ij}) have thus been determined according to Schrap and Opperhuizen (1989), and are listed in Table 5. No relative sorption coefficients, however, were determined for dried NZK sediment because of the small number of sorption coefficients available for this sediment. The relative sorption coefficients of the dried OVP sediment are approximately half of those in the wet sediment, but in general, the relative sorption coefficients appear to be relatively constant, independent on drying and on the type of sediment (Table 5). This implies that dried sediment can be used to study sorption and to compare the sorption coefficients of different organic compounds. The sorption coefficients of organic contaminants determined in dried sediment can thus be extrapolated to wet sediment, but it is essential to have measured the sorption coefficient of one of the compounds in the wet sediment, and the relative sorption coefficients in either wet or dried sediment.

Table 5. Relative sorption coefficients (R_{ij}) for wet and dried (300°C) OVP, RDD and NZK sediments, and for hexane pretreated NZK (NZK refluxed) sediment.

compound *i:* compound *j:*	pentaCBz 1234CBz	1234CBz 123CBz	pentaCN 2345CN	pentaCN pentaCBz
OVP wet	2.7	2.4	3.2	0.7
OVP dried	1.7	1.5	1.5	0.8
RDD wet	2.5	2.9	3.0	0.8
RDD dried	2.4	3.0	1.6	0.5
NZK wet	3.6	2.8	5.1	0.7
NZK dried	-	-	-	-
NZK refluxed	3.3	3.2	5.0	0.6
average (SD)	**2.7 (O.7)**	**2.6 (0.6)**	**3.2 (1.6)**	**0.7 (0.1)**

In summary, storage of OVP sediment at 5°C resulted in a decrease of the organic carbon content from 3.8% to 2.7% within 6 months, no further decrease was observed up to 94 months. Other sediment characteristics, such as inorganic carbon content, dry weight, nitrogen content, phosphorus content, iron content, manganese content and the fraction of particles <200 mm, did not change significantly during storage. Drying of the sediments at 200°C removed most of the hexane extractable background contamination and part of the organic carbon content, but did not affect the inorganic carbon content of OVP and KM sediments. Drying at 300°C, however, removed most of the organic carbon. The sorption coefficients of the test chemicals were significantly lower in dried (3OO°C) than in wet OVP, RDD and NZK sediment. The relative sorption coefficients, however, were not affected by drying. It is concluded that storage of sediment in the lab will affect the organic carbon content. Drying will also affect sediment and sorption characteristics, but has the advantage of removing background contamination. Using relative sorption coefficients makes extrapolation to wet sediments possible.

Acknowledgments. The Dutch Ministry of Housing, Physical Planning and Environment is thanked for their financial support. The National Institute for Coastal and Marine Management is thanked for determining the organic carbon of the OVP sediment after 94 months. We thank the chemical laboratories of the RIZA (IML) for characterizing the sediments.

REFERENCES

Banwart WL, A Khan and JJ Hassett (1980) Effect of sample pretreatment on sorption of acetophenone by soils and sediments. Environ Sci Health B15:165-179

Brusseau MC and PSC Rao (1989) The influence of sorbate-organic matter interactions on sorption non-equilibrium. Chemosphere 18:1691-1706

Capel PD and SJ Eisenreich (1990) Relationships between chlorinated hydrocarbons and organic carbon in sediment and porewater. J Great Lakes Res 16:245-257

Chiou CT, LJ Peters and VM Freed (1979) A physical concept of soil-water equilibria for nonionic organic compounds. Science 206:831-832

Chiou CT, PE Porter and DW Schmedding (1983) Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ Sci Technol I7:227-231

Grathwohl P (1990) Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons - Implications on K_{oc} correlations. Environ Sci Technol 24: 1687-1693

Gauthier TD, WR Seltz and CL Grant (I987) Effects of structural and compositional variations of dissolved humic materials on pyrene K_{oc} values. Environ Sci Technol 21:243-248

Karickhoff SW, DS Brown and TA Scott (1979) Sorption of hydrophobic pollutants on natural sediments. Water Res 13:241-248

Karickhoff, SW (1980) Sorption kinetics of hydrophobic pollutants in natural sediments. In: Baker RA (ed), Contaminants and Sediments, Vol 2; Ann Arbor Science, Ann Arbor Michigan, pp 193-206

Karickhoff SW and KR Morris (1985) Sorption dynamics of hydrophobic pollutants in sediment suspensions. Environ Toxicol Chem 4:469-479

Opperhuizen A (1986) Bioconcentration of hydrophobic chemicals in fish. In: Poston TM and R Purdy (eds), Aquatic Toxicology and Environmental Fate, Ninth Volume. American Society for Testing and Materials, ASTM STP 921, Philadelphia, pp 304-315

Rutherford DW, CT Chiou and DE Kile (1992) Influence of soil organic matter composition on the partition of organic compounds. Environ Sci Technol 26:336-340

Schrap SM and A Opperhuizen (1989) Quantifying the sorption of organic chemicals on sediments. Chemosphere 18:1883-1893

Schrap SM, PJ de Vries and A Opperhuizen (1994) Experimental problems in determining sorption coefficients of organic chemicals; an example for chlorobenzenes. Chemosphere 28:931-945

Schrap SM, M Haller and A Opperhuizen (1995) Investigating the influence of incomplete separation of sediment and water on experimental sorption coefficients of chlorinated benzenes. Environ Toxicol Chem 14:219-228

Sverdrup GM, BE Buxton, JC Chang and GS Casuccio (1990) Determination of optimal storage conditions for particle samples. Environ Sci Technol 24:1186-1195

Wable U, W Kördel and W Klein (1990) Methodology for the exposure assessment of soil for organic chemicals. Int J Environ Anal Chem 39:121.128

Xing B, WB McGill and MJ Dudas (1994) Sorption of alpha-naphthol onto organic sorbents varying in polarity and aromaticity. Chemosphere 28:145-153