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**Spatial and seasonal variations of Acid
Volatile Sulfide (AVS) and Simulta-
neously Extracted Metals (SEM) in
Dutch marine and freshwater sediments.**

M.A.G.T. van den Hoop, H.A. den Hollander,
H.N. Kerdijk*

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* Delft Hydraulics, Postbus 129, 9750 AC Haren.

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Rijksinstituut voor Volksgezondheid en Milieu, Postbus 1, 3720 BA Bilthoven
tel. 030-749111, fax 030-742971

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SUMMARY

Within the framework of the project Exposure Assessment, Acid Volatile Sulfide (AVS) and Simultaneously Extracted Metal (SEM) contents of Dutch marine and freshwater sediments were determined. For the present set of fifteen marine and six freshwater sediments AVS levels vary between non-detectable (<0.1) and approximately 50 μmol per gram dry sediment. The SEM/AVS ratio was found to be smaller than one in nineteen cases. Furthermore, seasonal variations in AVS and SEM concentrations were observed that may change the potential toxicity of metals in sediments. Seasonal changes in the SEM/AVS ratio were found to be different for various sediments.

SAMENVATTING

In het kader van het project Exposure Assessment zijn Acid Volatile Sulfide (AVS) en Simultaneously Extracted Metal (SEM) gehalten bepaald in een aantal mariene en zoetwater sedimenten. AVS-gehalten variëren van niet aantoonbaar (<0.1) tot ongeveer 50 μmol per gram droog sediment. In het merendeel van de monsters is een SEM/AVS ratio van kleiner dan 1 gevonden, hetgeen volgens recent gepubliceerde toxiciteitsonderzoeken inhoudt dat de metalen niet beschikbaar zijn voor opname door organismen. Het AVS gehalte blijkt onder andere afhankelijk te zijn van het jaargetijde, hetgeen kan leiden tot veranderingen in de potentiële beschikbaarheid van zware metalen.

1. INTRODUCTION

1.1 General

Within the framework of the project Exposure Assessment, the applicability of the equilibrium partitioning concept for the setting of “integrated environmental quality objectives” is investigated. A major assumption of the equilibrium partitioning concept is that the concentration of a chemical in water can be predicted from the concentration in the solid phase by using a measured or calculated equilibrium partitioning coefficient. For heavy metals, the partitioning behaviour generally depends on the physico-chemical characteristics of the natural system, such as redox potential, pH, content of clay and organic carbon, and, hence, it seems *a priori* impossible to obtain one single (universal) partition coefficient for various natural systems met in the environment.

To tackle this problem, one might try to obtain the best possible relationship between the partition coefficient and the (most) important system characteristics. For anaerobic sediments, it has been suggested that the acid extractable sulfide content plays a key role. The solubility of metal sulfide precipitates is very low, and under these conditions the partition coefficient may be simply related to the solubility product of the metal sulfide involved. Furthermore, toxic effects seem to be correlated with the amount of available sulfide present in the sediment. Under conditions of an excess of sulfide over metal, toxic effects appear to be absent due to the very low metal activity in the pore water. This means that large total concentrations of metal do not necessarily lead to poisoning of organisms (see section 1.2). Taking this into account, the Dutch quality criteria for heavy metals, which are based on total metal concentrations, are becoming subject of discussion at least for the anaerobic sulfide-rich sediments.

1.2 Acid Volatile Sulfide and toxic effects

Recently, much attention has been given to the importance of Acid Volatile Sulfide (AVS) as one of the major parameters with respect to the prediction of toxic effects of heavy metals in anaerobic sediments [1-6]. Acid Volatile Sulfide is an operationally defined parameter, which is a measure for the available amount of sulfide in the sediment. The general idea is that due to the very low solubility of heavy metal sulfide precipitates, heavy metals are not available for uptake by organisms in the presence of an excess of available sulfide. Di Toro *et al.* [1] have shown that lethal toxic effects of cadmium spiked marine sediment on amphipods can successfully be predicted by considering the Cd/AVS ratio, whereas estimation of the toxicity based on the total metal content of the sediment failed. Lethal toxic effects were found to be absent for Cd/AVS ratios smaller than one, but appeared to be present at Cd/AVS ratios exceeding one. Comparable results were observed for freshwater sediments [2], contaminated sediments with cadmium and nickel [3] and also with other organisms [4]. In all these studies toxic effects were found to increase significantly for metal/AVS ratios larger than one. Ankley *et al.* [5] have found that AVS alone is not always an appropriate partitioning phase for predicting metal bioavailability in freshwater sediments. For contaminated sediments with Cu/AVS ratios larger than one no lethal toxic effects were found on the amphipod *Hyalella azteca* in some cases. For

this particular case, an additional sorption phase may be important and, thus, normalization of copper concentrations to AVS in freshwater sediment may result in a conservative estimate of potential acute toxicity. Casas and Crecelius [6] have extended the investigations related to bioavailability of heavy metals in anoxic sediments and toxicity for the heavy metals zinc, lead and copper. The general pattern is that for simultaneously acid extractable metals (SEM) / AVS ratios smaller than one lethal toxic effects are absent.

1.3 Framework and aims

Within the project Exposure Assessment, so far attention has been paid to the item “AVS and SEM” in terms of a literature review [7] and the development of an analytical methodology for the determination of AVS and SEM contents in sediment and soil systems [8]. Most AVS levels reported in the literature are obtained mainly for marine sediments collected in the US and Canada [1-6]. Furthermore, little information is available with respect to series of acid extracted metals and AVS levels in sediments *under field conditions*. Our first goal was to study these parameters in both marine as well freshwater sediments in the Netherlands. Part of this work is carried out in collaboration with Delft Hydraulics in Haren, The Netherlands.

In addition, the production of AVS is mediated by sulfate-reducing bacteria [9], which reduce inorganic sulfate to sulfide. Hence, in the sediment the AVS content may vary among other things due to variations in biological activity, organic matter content, redox-conditions, and sulfate concentration. The accumulation of reduced inorganic sulfur products will be maximized in anoxic sediments with a sufficient source of sulfate and reduced carbon. Furthermore, it is expected that the biological process of sulfate-reduction will also depend on the temperature of the system and, thus, with the season. Our second objective was to examine the seasonal variability in AVS and SEM levels in sediment to determine if AVS and SEM measurements could be used predictably on a whole year basis.

2. MATERIALS AND METHODS

2.1 Sediment samples

Sediment samples (Figure 1; Table 1) were collected from Schoonrewoerdse Wiel, Botlek, Almere Waterwijk, Oostvaarders Plassen, Ketelmeer, Nieuwersluis (all freshwater sediments and analyzed in Bilthoven) and from Sluissche Hompels, Drempeel van Zandvliet, Geul Zandvliet/Barendrechtsluis, Drempeel van Lillo, Geul Boudewijn/van Cauwelaertsluis, Geul Kallosluis, Appelzak, Schouwen-Duivenland 1 and 4, Ter Heijden 2 and 4, Vlieland 4 and 70 and Terschelling 70 and 100 (all brackish or marine sediments and analyzed in Haren).

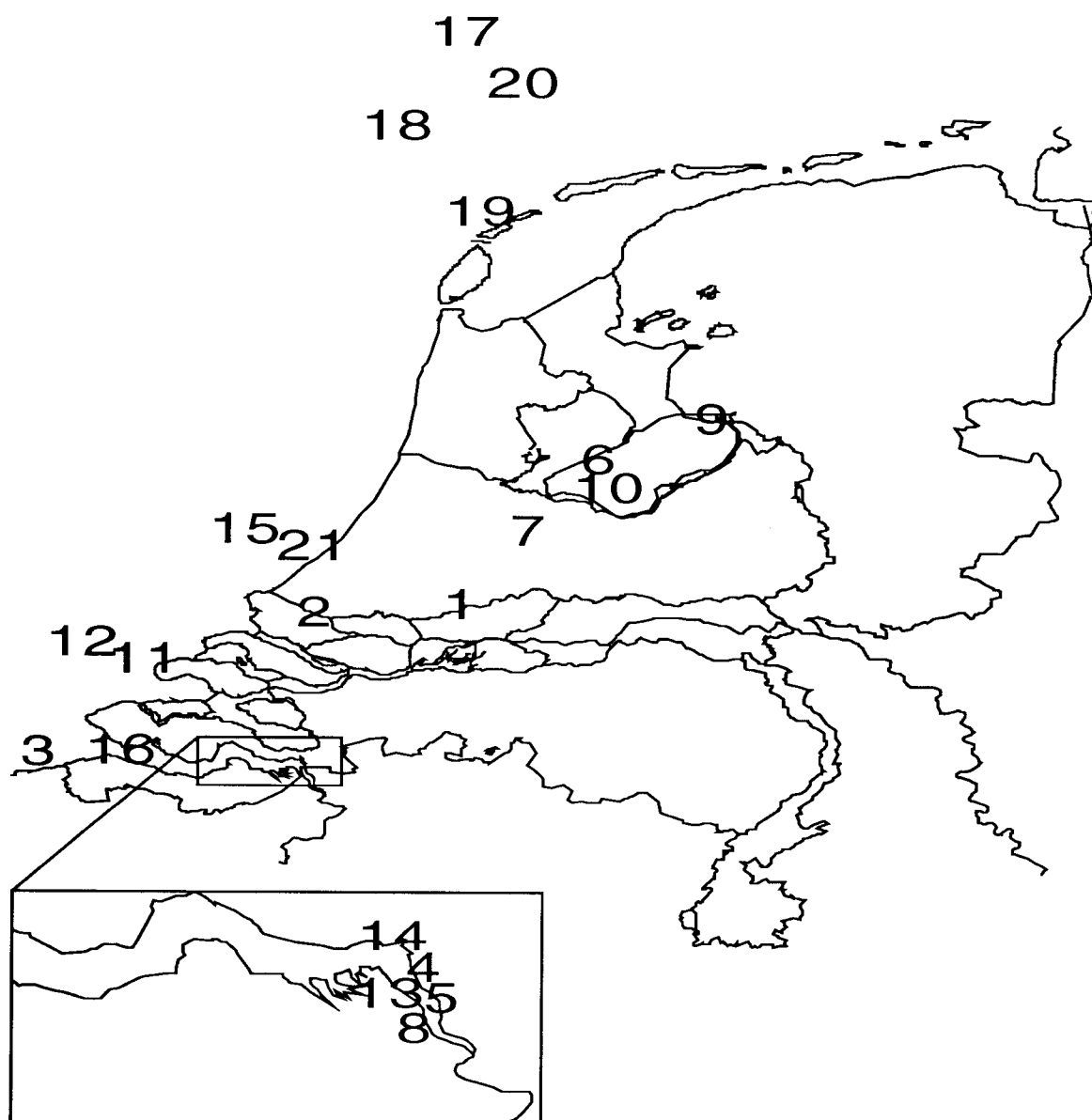


Figure 1: Sampling locations of Dutch marine and freshwater sediments. Sampling numbers are explained in Table 1.

In addition, two freshwater sediments were selected in order to study seasonal variability in AVS and SEM levels. One sediment was obtained from Almere Waterwijk (lake) in the Flevopolder. Samples were taken from a small creek, which is approximately 2 m wide. The thickness of the water layer varies from about 20 cm close to the land to approximately 50 cm in the middle of the creek. The second sample was obtained from Kromme Rijn at Odijk in the central of the Netherlands. Kromme Rijn is a small river (approximately 10 m wide) which is connected with the River Rhine. The sediments were monthly sampled starting Januari 1994 till Januari 1995. Samples of about 1/2 litre of sediment suspension were taken from the upper 10 cm within an area of approximately 1 square metre in order to minimize spatial heterogeneity effects. All collected samples were stored in the dark at 4°C until further analysis, which was usually carried out within a few days.

2.2 AVS and SEM analysis

For the Acid Volatile Sulfide and Simultaneously Extracted Metals determination a procedure was developed which is largely analogous to the one described by Allen *et al.* [10, 11]. In short, the experimental set-ups consist of a reaction vessel followed by one or two sequentially connected trapping vessels containing 100 ml of a 0.5 mol l⁻¹ sodium hydroxide solution. The sediment sample (5-10 gram of wet sediment) was added to 100 ml of deaerated Milli-Q-water in the reaction vessel. The suspension was stirred for 10 minutes while purging with deoxygenated, water-saturated nitrogen. After reducing the nitrogen flow to zero, 17 ml of 6 mol l⁻¹ hydrochloric acid was slowly added to the sediment suspension. Then the nitrogen flow rate was slowly increased to about 60 ml min⁻¹ and continued for at least 45 minutes. The sulfide concentration in the trapping vessels was determined colorimetric (Bilthoven) according to Kloster and King [12] or potentiometric (Haren) by adding Pb(NO₃)₂ and recording the potential. The resulting sediment suspension was centrifuged (Bilthoven) or filtrated (Haren). Cadmium, copper, nickel, lead and zinc in the supernatant/filtrate were determined by AAS. The recovery of the experimental set-up was checked by using a sodium sulfide solution with known concentration and appeared to be larger than 90%. For duplicate measurements, the mean relative variation of the AVS-content and SEM-content were found to be approximately 7 and 3%, respectively.

3. RESULTS AND DISCUSSION

3.1 Spatial AVS and SEM patterns

Acid Volatile Sulfide levels of Dutch freshwater and marine sediments vary between non-detectable (<0.1) and approximately 50 μmol per gram dry sediment (see Table 1). This is in line with literature values reported for marine and freshwater sediments in the US and Canada, which were found to range from 2 up to 40 μmol per gram dry sediment (see Table 2). Relatively small AVS levels (<2 $\mu\text{mol g}^{-1}$) have been found only for six marine sediments. Obviously, the lower sulfate concentration which is usually observed in freshwater sediments compared to marine systems, is not a limiting factor in the “production” of AVS. About 50% of the presently investigated samples have an AVS level of more than 10 $\mu\text{mol g}^{-1}$. Hence, these sediments are able to bind heavy metals in large quantities.

Table 1: AVS, acid extractable heavy metal and SEM levels (all in $\mu\text{mol g}^{-1}$) and the resulting SEM/AVS ratio for some Dutch freshwater and marine sediments, listed in order of decreasing AVS-levels. The number of the sample refers to the sampling site which is presented in figure 1.

Sample (number/site)	AVS	Cd	Cu	Ni	Pb	Zn	SEM	SEM/AVS
1 Schoonrewoerdse wiel	52.0	0.018	0.33	0.46	0.44	2.42	3.67	0.07
2 Botlek	22.6	0.055	0.78	0.39	0.62	7.50	9.35	0.41
3 Appelzak	22.6	0.004	0.04	0.04	0.12	0.88	1.08	0.05
4 Geul Zandvliet /Berendrechtsluis	21.2	0.066	0.42	0.23	0.61	6.97	8.30	0.39
5 Geul Boudewijn v Cauwelaertsluis	20.0	0.063	0.34	0.22	0.62	8.52	9.76	0.49
6 Oostvaarders Plassen	19.9	0.006	0.17	0.21	0.25	1.88	2.52	0.13
7 Nieuwersluis	19.8	0.004	0.10	0.16	0.36	2.32	2.94	0.15
8 Geul Kallosluis	18.4	0.063	0.53	0.26	0.68	7.84	9.37	0.51
9 Ketelmeer	16.4	0.067	1.13	0.46	0.63	11.91	14.20	0.87
10 Almere Waterwijk	15.1	0.003	0.02	0.13	0.06	0.35	0.56	0.04
11 Schouwen-Duiveland 1 ^a	8.0	0.001	0.02	0.02	0.04	0.32	0.40	0.05
12 Schouwen-Duiveland 4 ^a	7.4	0.001	0.01	0.02	0.03	0.26	0.32	0.04
13 Drempel van Lillo	4.7	0.021	0.35	0.09	0.24	3.11	3.81	0.81
14 Drempel van Zandvliet	4.1	0.007	0.08	0.04	0.08	1.07	1.28	0.31
15 Ter Heijden 4 ^a	2.9	0.001	0.04	0.02	0.06	0.47	0.59	0.20
16 Sluissche Hompels	1.3	0.001	0.03	0.02	0.03	0.39	0.47	0.36
17 Terschelling 100 ^a	0.6	<0.001	0.02	0.02	0.04	0.24	0.32	0.53
18 Vlieland 70 ^a	0.5	<0.001	0.02	0.02	0.05	0.40	0.49	0.98
19 Vlieland 4 ^a	0.4	<0.001	0.01	0.01	0.01	0.13	0.16	0.40
20 Terschelling 70 ^a	0.2	<0.001	0.02	0.02	0.05	0.40	0.49	2.45
21 Ter Heijden 2 ^a	<0.1	<0.001	0.02	<0.01	0.02	0.26	0.31	>3.1

^a Number refers to the sampling distance in kilometres perpendicular on the coast line.

Table 2: AVS and SEM levels for sediments from the US and Canada as reported in the literature.

range of AVS $\mu\text{mol g}^{-1}$	metals studied	SEM/AVS	type of experiment	number of samples	reference
0.1-75.5	Cd/Ni	0.1-218	toxicity	17	[3]
3.6-42.0	Cd (added)	-	toxicity	3	[2]
2.3-175	Cd (added)	-	toxicity	4	[1]
0.4-3.6	n.d. ^a	-	field study ^b	3	[13]
0.3-11.6	Cu	0.2-17500	toxicity	22	[5]
1.7-24.2	Cd/Cu/Ni/Zn	0.3-14	analytical	4	[10]
1.9-50.5	Cu/Pb/Zn (added)	0.1-3.0	toxicity	3	[6]

^a n.d. = not determined;

^b field study with respect to seasonal and spatial changes of AVS levels in an anoxic mesotrophic lake.

Acid extractable metal concentrations differ considerably from sediment to sediment. In all cases acid extractable heavy metal concentrations increase in the range $\text{Cd} < \text{Cu} < \text{Pb} < \text{Zn}$. Nickel is found to be present in quantities larger than Cd but smaller than Pb and Zn. No clear relationship is observed between the nickel and copper concentrations. Zinc accounts for approximately 80 % of the total amount of acid extractable metals, whereas the contribution of the much more toxic cadmium to SEM is less than one percent. Nickel sulfide is the most "soluble" precipitate of the heavy metals considered in the present study, followed by zinc sulfide (see Table 3). Taking this into account one might expect that for Dutch sediments with SEM/AVS ratios larger than one, nickel and zinc will be the heavy metals with relatively high concentration in the pore water and, thus, will be available for uptake by organisms.

Table 3: Solubility products (K_s) of various metal sulfides [14].

Metal sulfide	Log K_s	Metal sulfide	Log K_s
MnS	-13.33	PbS	-28.04
FeS	-18.80	CdS	-28.85
NiS	-20.97	CuS	-35.90
ZnS	-24.53	α -Ag ₂ S	-49.17
SnS	-27.49	HgS (black)	-52.19

The sum of the five simultaneously extracted metals (SEM) is found in the range 0.16 to 14.2 μmol per gram dry sediment. According to Di Toro *et al.* [4] no lethal toxic effects are expected if the SEM/AVS ratio is smaller than one. Most sediments analyzed have a SEM/AVS ratio smaller than one (see Table 1). For the samples, Ter Heijden 2 and Terschelling 70, the SEM/AVS ratio is found to be larger than one. The SEM/AVS ratio of Vlieland 70 is approximately 1. The fractions of organic matter and clay of these samples have been found to be very small $< 0.7\%$ and $< 5\%$, respectively. Total Cd, Cu, Pb and Zn contents of these

samples are in the order of 0.04, 4, 7 and 26 mg kg⁻¹. These values correspond with background levels in Dutch soils collected from areas which are thought to be least influenced by human activities [15]. Hence, it is expected that the determined SEM/AVS ratios in these three sediments will not result in toxic effects to organisms. Finally, the sediment from Ketelmeer is known to be highly contaminated with heavy metals and organic pollutants. Since the SEM/AVS ratio for this sample is found to be smaller than one, toxic effects observed in laboratory or field studies may be more related to the occurrence of organic pollutants than to heavy metals.

3.2 Seasonal AVS and SEM patterns

For the Waterwijk and Kromme Rijn sediment, monthly determined AVS and SEM levels are presented in figures 2a and b, respectively. For the Waterwijk sediment, a nearly constant AVS level of approximately 1 µmol per gram dry sediment is observed from Februari till August, whereas increased AVS levels are found from August till Januari. The results are in line with the observations for an anoxic mesotrophic lake [13]. A similar trend has been observed too for sulfide pore water concentrations [16-18]. For the present sediment, SEM levels are found to be approximately constant during the year and appear to be about 0.45 ± 0.19 µmol per gram dry sediment.

For the Kromme Rijn sample, seasonal AVS and SEM patterns are quite different from the ones observed for the Waterwijk sediment. First, there is no clear relationship between AVS level and sampling time. AVS-levels vary from 6.6 up to 37.7 µmol per gram dry sediment. Secondly, SEM levels vary considerably too over the year. In fact, SEM levels seem to follow the AVS pattern, which becomes clear if one considers the SEM/AVS-ratio (see Table 4). For the Kromme Rijn sample a nearly constant SEM/AVS ratio is found (0.42) with a small deviation (0.06), whereas the deviation in the SEM/AVS ratio for the sediment from Waterwijk is in the same order of magnitude as the average value. The AVS pattern of the Kromme Rijn sediment might be related with the dynamic behaviour of the water stream. The velocity of surface water in the river is fast (at least on a visual basis), which might result in transportation of the sediment. Therefore, the observed AVS and SEM patterns might reflect more the spatial heterogeneity of the sediment along the river rather than seasonal influences. Another indication is that the SEM content varies considerably for the Kromme Rijn sample, whereas the SEM content of the Waterwijk sediment (where no visual water transport is) appears to be fairly constant.

Table 4: Seasonal SEM/AVS ratios for the Waterwijk and Kromme Rijn sediment (Jan 1994 till Jan 1995).

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	mean	standard deviation
Waterwijk	0.24	0.97	0.49	0.21	0.49	0.23	0.58	0.04	0.07	0.18	0.05	0.16	0.31	0.28
Kromme Rijn	0.49	0.45	0.44	0.29	0.41	0.48	0.45	0.32	0.48	0.43	0.39	0.38	0.42	0.06

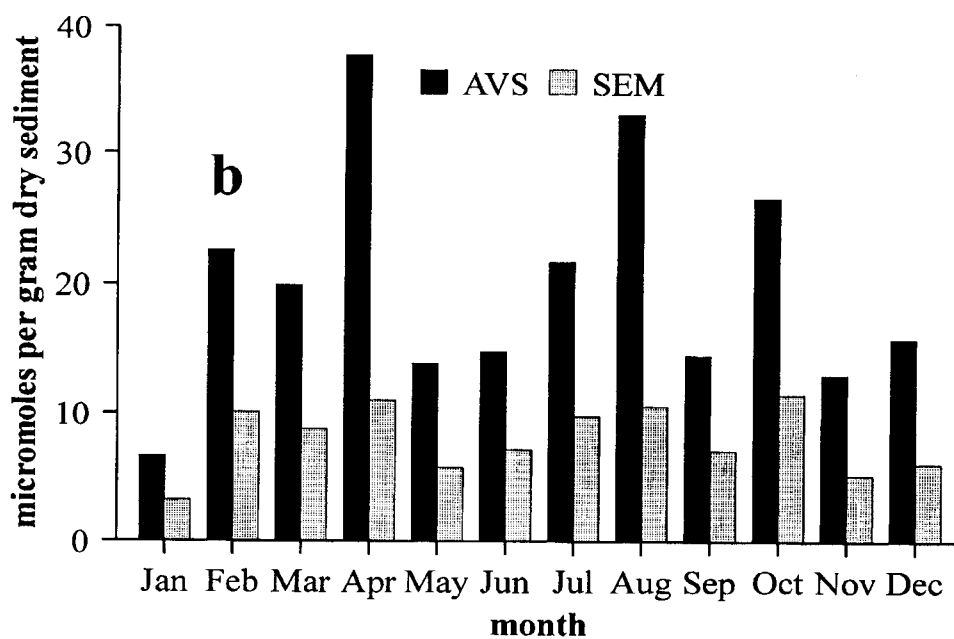
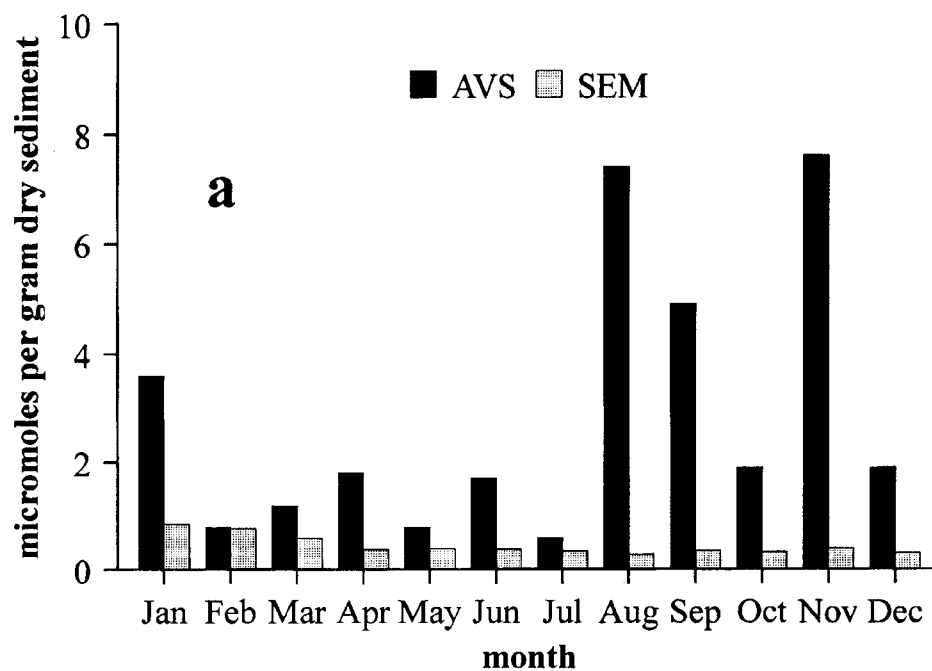


Figure 2: Seasonal AVS and SEM concentrations in the Waterwijk (a) and Kromme Rijn (b) sediment, respectively, for 1994.

AVS levels appear to vary during the year. For constant SEM-values, this will lead to changes in the SEM/AVS ratio and, hence, in the availability of the heavy metals for organisms. The Waterwijk sediment seems to be a typical example illustrating the described pattern. For example, the SEM/AVS ratio decreases to nearly zero in August, whereas in Februari the SEM/AVS ratio approaches a value of one. For this type a sediment, it seems impossible to predict from one single measurement the SEM/AVS pattern for a whole year. In this particular case, sampling in August may lead to an overestimation of the buffering capacity of the sediment. On the other hand, for the case of the Kromme Rijn sample, the SEM/AVS ratio appears to be nearly constant over time. Hence, for this type of sediments, a single measurement of the AVS and SEM level seems to be enough to predict the SEM/AVS-ratio pattern for a whole year.

4. CONCLUSIONS

- 1) AVS-levels in Dutch marine and freshwater sediments vary from non-detectable up to 50 μmol per gram dry sediment, which is in line with values reported for samples from the US and Canada.
- 2) For most sediments SEM/AVS ratios are found to be smaller than 1. Hence, the metals are expected not to be available for uptake by organisms considering the recently published studies on toxicity in relation to availability expressed as SEM/AVS-ratios for these types of systems.
- 3) Seasonal variations in AVS concentration were observed that may change the potential toxicity of metals in sediments. For sediments with a constant SEM level, it seems impossible to predict the SEM/AVS pattern for a whole year on the basis of one single measurement. However, the results show that other types of sediments exist with constant SEM/AVS ratios during the year.

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