

# **European Union Risk Assessment Report**

## **CADMIUM METAL AND CADMIUM OXIDE**

CAS-No.: 7440-43-9 and 1306-19-0  
EINECS-No.: 231-152-8 and 215-146-2

### **RISK ASSESSMENT**

#### **ADDENDA TO PART I – ENVIRONMENT**

#### **STAGE II: CONCLUSION (I)**

#### GENERAL NOTE

This document contains two different addenda:

- Stage II: Conclusion (i) **toxicity in very soft water** (19 pages)
- Stage II: Conclusion (i) **bioavailability in sediment** (66 pages)

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### **RISK ASSESSMENT**

#### **STAGE II: CONCLUSION (I) TOXICITY IN VERY SOFT WATER**

Addendum to Part I - Environment (2007)

May 2008

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## EXPLANARY NOTE

This report is an addendum to the European Risk Assessment Report (RAR) on cadmium and cadmium oxide that has been prepared by Belgium in the context of Council Regulation (EEC) No. 793/93 on the evaluation and control of existing substances and published in 2007 on the European Chemicals Bureau Website (European Risk Assessment Report Vol.72, EUR 22919 EN)<sup>1</sup>.

In the frame of this work, the environmental risk assessment for cadmium and cadmium oxide was completed with a **conclusion (i)** for the aquatic compartment. There was felt to be a need for further toxicity testing to assess risks of Cd in very soft waters. Consequently, chronic Cd toxicity to fish and invertebrates was assessed in various soft waters. Results are presented in this report.

For detailed information on the risk assessment principles and procedures followed, the underlying data and the literature references, the reader is referred to the Risk Assessment Report.

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<sup>1</sup> European Chemicals Bureau – Existing Chemicals – <http://ecb.jrc.ec.europa.eu/>

## **OVERALL RESULTS OF THE RISK ASSESSMENT - ADDENDUM**

CAS Number: 7440-43-9 and 1306-19-0  
EINECS Number: 231-152-8 and 215-146-2  
IUPAC Name: cadmium metal and cadmium oxide

### **Environment – Aquatic compartment**

**Conclusion (ii)** There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

This conclusion was reached because no risk is predicted for aquatic organisms in the soft waters (hardness below 40 mg CaCO<sub>3</sub>/L) of the Swedish region for which a characterization was made with the hardness corrected PNEC. The risk is uncertain for other soft water regions for which a risk characterization was not made. The risk is also uncertain outside the range of the water characteristics on which the soft water PNEC is based, that is below hardness 5 mg CaCO<sub>3</sub>/L, i.e. extremely soft waters.

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## 1 INTRODUCTION – OBJECTIVES OF FURTHER TESTING

The environmental risk assessment for cadmium and cadmium oxide was completed with a **conclusion (i)** for the aquatic compartment (EC, 2007). There was a need for further testing to assess risks of Cd in very soft waters. The reasoning behind was the following: the Risk Assessment Report (RAR) on cadmium and cadmium oxide derived a generic PNEC of 0.19 µg/L. Hardness affects Cd toxicity and a hardness dependent regional PNEC was derived. Three chronic studies were available that yielded a relationship between the toxicity (NOEC and LOEC) and hardness. This relationship was only valid between hardness H=40-250 mg CaCO<sub>3</sub>/L. Based on this relationship and the assumption not to extrapolate outside this hardness range, a regional, hardness specific PNEC was derived as

$$\text{PNEC}_{\text{water,regional}} = 0.09 (H/50)^{0.74} \quad (\text{in } \mu\text{g/L})$$

or, in table form (see Table 1.1):

Table 1.1. The regional PNEC of Cd in water as a function of water hardness as used in the RAR Cd/CdO

Hardness (mg CaCO <sub>3</sub> /L)	PNEC <sub>water</sub> µg Cd/L
H<40	0.08
H 40	0.08
H 50	0.09
H 100	0.15
H 200	0.25

The relationship between toxicity (log transformed) and hardness (in mg CaCO<sub>3</sub>/L, log transformed) is termed the hardness slope and this value is 0.74. However, the RAR of Cd/CdO concluded that further testing was required to assess risks of Cd in *very soft* water, i.e. water with hardness below 40 mg CaCO<sub>3</sub>/L. Surveys indicate that northern European countries have more than 10% of the sampled locations with hardness below about 10 mg CaCO<sub>3</sub>/L. Waters of this character also exists at some other locations in Europe. Therefore, a **conclusion (i)** programme was started that assessed chronic Cd toxicity to fish and invertebrates in various soft waters in which hardness was artificially increased from background to H=10 and H=40 mg CaCO<sub>3</sub>/L. This study effectively assesses a new hardness slope between very soft water (hardness 1-2 mg CaCO<sub>3</sub>/L) and water with a hardness 40 mg CaCO<sub>3</sub>/L. The BLM concept predicts that there should not be a continuous increase in Cd toxicity with decreasing hardness since Cd becomes increasingly better complexed with dissolved organic matter with decreasing hardness.

The agreed conclusion (i) programme involved:

- (1) Cd toxicity to *Daphnia longispina* in 3 different very soft waters that were each modified from background to H=10 and H=40 mg CaCO<sub>3</sub>/L, i.e. 3\*3 tests;
- (2) An early life stage test with *Salmo trutta* (brown trout) in 1 water modified from background to H=10 and H=40 mg CaCO<sub>3</sub>/L, i.e. 3 tests;
- (3) No tests with algae since these species were found to be relatively insensitive to Cd; however, a study, not sponsored by industry, was performed during the conclusion (i) programme and this fulfilled the conceptual needs, i.e. toxicity of Cd in different waters with hardness modified from background to H=10 and H=40 mg CaCO<sub>3</sub>/L.

## 2 CHRONIC TOXICITY TO AQUATIC ORGANISMS IN VERY SOFT WATER

### Tests with *Daphnia longispina*

The summary of the results (UG, 2007) is given in Annex 1. The tests yielded reliable data in 2 waters at all hardness values tested whereas control mortality (30-50%) and reproduction were unacceptable for reliable dose-response studies in the third water. The data are summarized in Table 2.1

Table 2.1. Hardness (H, in mg CaCO<sub>3</sub>/L; measured) effects for Cd toxicity to *D. longispina*. The 95% confidence limits of EC10 are given in brackets. A positive value of the hardness slope means decreasing toxicity with increasing hardness. n.s.=no significant effect of hardness on the toxicity threshold based on statistical analysis of the original report.

Threshold	Lake Maridalsvann	Lake Sandungen
EC10 (µg/L)	H=7.5: 0.46 (0.08-2.6) H=12.5: 0.29 (0.06-1.5) <sup>n.s.</sup> H=38.5 0.93 (0.51-1.7) <sup>n.s.</sup>	H=5.5: 1.6 (0.67-3.8) H=12 0.58 (0.27-1.3) <sup>n.s.</sup> H=46 0.79 (0.21-2.7) <sup>n.s.</sup>
Hardness slope <sup>2</sup>	0.53 <sup>n.s.</sup>	-0.27 <sup>n.s.</sup>
EC50 (µg/L)	H=5.5 3.9 (2.3-6.1) H=12.5 3.5 (2.0-6.1) <sup>n.s.</sup> H=38.5 3.6 (2.8-4.6) <sup>n.s.</sup>	H=5.5 4.3 (2.9-6.4) H=12 3.9 (3.0-5.2) <sup>n.s.</sup> H=46 7.3 (4.4-12) <sup>n.s.</sup>
Hardness slope <sup>2</sup>	-0.04 <sup>n.s.</sup>	0.27 <sup>n.s.</sup>

### Tests with *Salmo trutta*

The summary of the results (NIVA, 2007a) is given in Annex 2. The tests yielded reliable data at all hardness values tested. The data of the most sensitive endpoint (weight at start feeding) are summarized in Table 2.2. No EC50 values can be estimated because of small effects found. The EC10 values are highly dependent on the statistical analysis of the data because of small overall effects of Cd (maximally 24% inhibition). The author of the report states: '*The dose-response relationship for weight at start feeding towards water cadmium is not very clear... Furthermore, as a consequence of the method-dependent EC10 values for medium water hardness the effect of water hardness on the EC10 values also vary according to the method used for fitting the dose-response curves...Still, it can be concluded that the effect of water hardness on weight at start feeding EC10 in brown trout is highly significant between 2.7 and 42.7 mg CaCO<sub>3</sub>/l, but that the response pattern between these hardness levels remains enigmatic*' (Thron Hagen, pers. comm.. 19 Sept.2007)

<sup>2</sup> Hardness slope: slope of log transformed toxic threshold to log transformed measured water hardness level



Table 2.2. Hardness (H, in mg CaCO<sub>3</sub>/L; measured) effects for Cd toxicity to *S. trutta*. Means followed by the same character are statistically significant based on statistical analysis of the original report.

Threshold	Lake Bygladsforden H= 2.7 mg CaCO <sub>3</sub> /L	
EC10 (µg/L)	by unweighted regression	weighed regression (95% CI), selected here
H=2.7	0.52	0.35 (0.25-0.47) <sup>a</sup>
H=12.8	5.25	0.91 (0.38-2.24) <sup>ab</sup>
H=42.7	7.00	5.70 (1.9-19.8) <sup>b</sup>
Hardness slope <sup>2</sup>	0.97	0.99
LOEC (µg/L)		
H=2.7	0.95	
H=12.8	3.1	
H=42.7	3.1	
Hardness slope <sup>2</sup>	0.44 <sup>*</sup>	

#### Tests with *Pseudokirchneriella subcapitata*

The tests with algae (NIVA, 2007b) yielded reliable EC10 and EC50 values as a function of water hardness in one water. Data on the other water were not used since EDTA was added to the media and these data were considered unreliable for the purpose of the risk assessment. Data are summarized in Table 2.3.

Table 2.3. Toxicity thresholds for Cd to *P. subcapitata*. The 95% confidence limits are given in brackets. Statistical tests (\*=P<0.05; n.s. P>0.05) based on statistical analysis of the original report. (H, in mg CaCO<sub>3</sub>/L; measured)

Threshold	Lake Sandungen H= 6.2 mg CaCO <sub>3</sub> /L
EC10 (µg/L)	
H=6.2	7.5 (5.5-10.2)
H=16.2	8.5 (7.1-10.2) <sup>n.s.</sup>
H=42.7	6.0 (3.5-11.6) <sup>n.s.</sup>
Hardness slope <sup>2</sup>	-0.11 <sup>n.s.</sup>
EC50	
H=6.2	29 (26-35)
H=16.2	41 (37-44) <sup>*</sup>
H=42.7	199 (158-265) <sup>*</sup>
Hardness slope <sup>2</sup>	0.97 <sup>*</sup>

<sup>2</sup> Hardness slope: slope of log transformed toxic threshold to log transformed measured water hardness level

Discussion and derivation of a PNEC for very soft waters with H<40 mg CaCO<sub>3</sub>/L.

Table 2.4 summarizes the hardness effects noted. The *D. longispina* test showed no effects of hardness, the fish test showed a significant effect of hardness between H=2.7 and H=42.7 but pairwise t-tests between low and medium or between medium and high hardness did not reveal significant differences. The tests with algae showed no significant effect of hardness at EC10 level but demonstrated a hardness effect at EC50 level. The *average* hardness slopes of the 4 tests are not significantly different from zero, neither at EC10, nor at EC50/LOEC. The conclusion of that exercise is that the *average* slopes of hardness effects on Cd toxicity between H=3-43 mg CaCO<sub>3</sub>/L (0.14-0.41) are smaller than the slope previously found between hardness 40-200 mg CaCO<sub>3</sub>/L. (0.74). The explanation for this lower slope is that Cd binding to dissolved organic matter (DOM) becomes increasingly more important at lower hardness which cancels out the hardness effects on the free ion (Cd<sup>2+</sup>) toxicity.

Table 2.4. Summary of hardness effects on Cd toxicity for *D. longispina* (2 waters), *S. trutta* (1 water) and *P. subcapitata* (1 water) between hardness H=2.7-53 mg CaCO<sub>3</sub>/L. Positive effects and positive values for a slope mean that the toxicity decreases with increasing hardness.

Threshold	Hardness effects				Hardness slope
	n	positive effects	no significant effects	negative effects	average slope (95% confidence limit)
EC10	4	1	3	0	0.28 (-0.65 to 1.21) <sup>n.s.</sup>
EC50 (or LOEC for fish test)	4	2	2	0	0.41 (-0.26 to 1.08) <sup>n.s.</sup>

The adjustment for the PNEC is preferentially set using the slope at EC10/NOEC level since the PNEC is based on NOEC/EC10 levels itself. The consequence for choosing this hardness slope (0.28) is given in Table 2.5.

Table 2.5. Illustration how PNEC can be affected by water hardness if the PNEC previously agreed for water with H=40 is adjusted with the average slope (0.28) for hardness in soft water based on EC10 or NOEC values.

Hardness H (mg CaCO <sub>3</sub> /L)	PNEC=0.08*(H/40) <sup>0.14</sup> µg/L
40	0.080
20	0.066
10	0.054
5	0.045
2.5	0.037

The new slope changes the PNEC about a factor 2 between the H=40 and H=2.5.

It is proposed not to use this slope and keep the PNEC=0.08µg Cd/L for all waters with hardness below H=40 mg CaCO<sub>3</sub>/L for the following reasons:

1. All EC10 or NOEC values of the 12 reliable tests in very soft waters are above the current PNEC for soft water which is 0.080 µg/L. The lowest among the 12 EC10 values is 0.29 µg Cd/L and the average EC10 value is 1.15 µg/L.
2. The invertebrates are the most sensitive species for Cd (lowest NOEC values), i.e. they have largest impact in the PNEC and the effects of hardness on invertebrates were insignificant in the very soft waters.

3. The *average* hardness slope that is used to adjust the PNEC is not significantly different from zero.
4. The effect of water hardness on the PNEC with the lower slope has only a small effect on the PNEC (about a factor 2 down to very soft water of H=2.5).
5. The modified PNEC for very soft water of H=2.5 is 0.037 µg Cd/L this value is set in the uncertainty range of detection. Moreover, this value is below the Cd concentrations in the control of the tests, taking the variation of control Cd into account. For example, the report of the invertebrate testing reported that their analysis with ICP-MS has an instrument detection limit of 0.001 µg/L. However, all steps involving sample treatment (e.g., filtering), storage and analysis (including matrix effects) increases the true limit of detection (LOD) and the limit of quantification (LOQ) to 0.010 µg/l and 0.032 µg/l, respectively. The raw data provided by the authors showed that standard deviations of replicate analyses of the control waters during the tests (i.e. new&old waters after renewals) were, on average, 0.037 µg/L, at the modified PNEC for very soft water of H=2.5. In the fish tests, standard deviations of replicate analysis of the control waters during the tests were smaller (0.004-0.017 µg/L) but the range of Cd concentrations in the different control solutions (means of each tank ± standard deviation) is up to 0.042 µg/L i.e. exceeding the modified PNEC for very soft water.
6. The RAR on Cd/CdO already concluded that there were sufficient data of Cd toxicity tested in soft waters with hardness between H= 10 and 40 mg CaCO<sub>3</sub>/L, including mesocosm studies at hardness of about 10 and that justified that the lowest PNEC at H=40, i.e. 0.08µg Cd/L was sufficiently protective for waters with hardness as low as H=10 mg CaCO<sub>3</sub>/L.

This conclusion is obviously limited by the information gathered here and consequently this conclusion should not be used outside the range of water characteristics on which it is calibrated.

This range is:

- Hardness: between 2.7 and 47 mg CaCO<sub>3</sub>/L with the additional note that the most sensitive species (invertebrates) were not tested below a hardness of about 5 mg CaCO<sub>3</sub>/L since the test in the softest water (hardness 1-4 mg CaCO<sub>3</sub>/L) failed.
- DOC: between 2 and about 8 mg C/L with the additional note that the most sensitive species was only tested at DOC concentrations ranging between 4-8 mg/L during the test. In theory, a lower DOC concentration could provoke a stronger hardness effect (as predicted based on a BLM concept), however trace metal deficiency (e.g. Fe) may also become more important stress factors at lower DOC concentrations with unknown net effects on Cd toxicity.

### Conclusion

No further adjustment of the PNEC in very soft water is necessary and the previously agreed regional **PNEC of 0.08 µg/L** (Table 1.1) is proposed for waters with hardness 2.7-40 mg CaCO<sub>3</sub>/L and DOC concentrations above 2 mg C/L with the additional warning that for the most sensitive species there is no information that there would be no adverse effects below that PNEC below hardness 5 mg CaCO<sub>3</sub>/L and DOC 4 mg/L.

### 3 RISK CHARACTERISATION

#### Regional and continental Cd concentrations:

*Measured values:* a risk characterisation for soft water is possible for the set of data that allow a 'bioavailability correction', i.e. a correction of the PNEC based on water hardness. However, it was only possible to make such corrections for water hardness for the dataset of Sweden. In that case, risk factors were calculated for each monitoring point as the ratio of PEC to the hardness corrected PNEC. The 90<sup>th</sup> percentile of these risk factors is below 1 and is represented in the Table 3.1.

Table 3.1. Regional risk characterisation for water in a dataset where water hardness and Cd concentrations are coupled.

The factor risk = PEC/PNEC. The PNEC<sub>water</sub> includes bioavailability corrections (hardness correction). Data refer to period 1995-2001.

Country	n	P90 of Cd [µg L <sup>-1</sup> ]	Hardness mg CaCO <sub>3</sub> L <sup>-1</sup>	Factor risk	
				P90 of risk factors	Average of site specific P90
Sweden <sup>3</sup> data of hardness >5 mg CaCO <sub>3</sub> /L	7360 (44 sites)	0.058	5->1000	0.66	0.50

The risk factor for the Swedish data with RI=1 is 0.66. This risk factor is obtained after correction for water hardness, using the formula for water hardness correction as presented in section 1, down to hardness 40 mg L<sup>-1</sup> and using the proposed PNEC<sub>water</sub> for soft waters (from 40 mg L<sup>-1</sup> down to 5 mg L<sup>-1</sup> CaCO<sub>3</sub>) of 0.08 µg Cd L<sup>-1</sup>. Uncorrected, the risk factor would become 0.22. As the corrected risk factor is much higher than the uncorrected one, it is advisable to use values corrected for water hardness for soft waters, when available. The PNEC<sub>water</sub> for the extremely soft waters (H below about 5 mg CaCO<sub>3</sub>/L; about 10% of the data) is uncertain and these areas may be unprotected by the proposed PNEC<sub>water</sub> for soft water (0.08 µg Cd L<sup>-1</sup>). In conclusion, there is no risk for the majority of the Swedish region for which a characterization was made.

<sup>3</sup> Data were gathered by the Swedish University of Agricultural Sciences and can be consulted on the web at <http://info1.ma.slu.se/>.

#### 4 REFERENCES

EC (2007). Cadmium and cadmium oxide. European Union Risk Assessment Report, Vol.72. European Commission (EC), Publication No. EUR 22919 EN (Internet publication at <http://ecb.jrc.it/>).

NIVA (2007a). Study of the effect of Cd on the early life stages of brown trout *Salmo trutta* at different levels of water hardness. Haugen et al., 2007, Norwegian Institute for Water Research, report 5468-2007.

NIVA (2007b). Effect of water hardness on the toxicity of cadmium to the alga *Pseudokirchneriella subcapitata*; Torsten Källqvist, 2007. Norwegian Institute for Water Research, Report 5422-2007.

UG (2007). Chronic ecotoxicity of cadmium to *Daphnia longispina* exposed in very soft surface water; Messiaen M. et al., University of Gent, Belgium.

## ANNEXES

### Annex 1. The toxicity of Cd to *D. longispina* in very soft waters

(report: Chronic ecotoxicity of cadmium to *Daphnia longispina* exposed in very soft surface water; Messiaen M. et al., University of Gent, Belgium)

#### Brief test description

Three Norwegian soft surface waters were sampled in December 2006, i.e. Lake Byglandsfjorden, Lake Sandungen and Lake Maridalsvann. Two hundred liters of were collected and shipped to Ghent University in January 2007 for the acclimation and toxicity testing research. The hardness was adjusted to H=10 and/or H=40 by adding a solution of CaCl<sub>2</sub>.2H<sub>2</sub>O and MgCl<sub>2</sub>.6H<sub>2</sub>O, while respecting the naturally occurring Ca/Mg ratio. This research was performed using a laboratory *Daphnia longispina* clone which was originally collected from a pond in Sweden. Before initiation of the acclimation period, a single clone was isolated from the laboratory population. In a first phase, the *D. longispina* clone was acclimated to the three natural waters as well as to the six waters with adjusted hardness (i.e. nine waters in total). Acclimation lasted a total of 6 weeks and covered 2 generations. The organisms were fed daily with a mixture of the algae in a 3:1 ratio of *Pseudokirchneriella subcapitata* and *Chlamydomonas reinhardtii*. Daphnids taken from the second acclimation generation were used as test organisms in the toxicity tests that followed test protocol OECD 211. The Cd was added in 7 concentrations, each varying a factor 1.8, starting from 0.32 µg Cd/L-1 µg/L depending on the water. Water characteristics were measured during the test at regular occasions and toxicity thresholds refer to average measured values during the test. Results are given in Table A1. Tests in Lake Byglandsfjorden were considered unreliable by the authors since control mortality was largest (30-50%) and reproduction too variable. Reproduction was in general the most sensitive endpoint and the toxicity thresholds of this endpoint were chosen here for indicating hardness effects. On the basis of six successful chronic toxicity experiments with fully acclimated *Daphnia longispina* in two natural surface waters, the authors concluded that the effect of water hardness on chronic Cd toxicity to *D. longispina* is not significant between 5.8 and 46 mg CaCO<sub>3</sub>/L.

Table A1 Summary of test results with *D. longispina*. Confidence limits of EC10 and EC50 are given in brackets. Statistical tests (\*=P<0.05; n.s. P>0.05) are contrasts with control (=softest) water.

Parameter	Lake Byglandsfjorden	Lake Maridalsvann	Lake Sandungen
Lake water			
H (mg CaCO <sub>3</sub> /L)	1.2	6.2	5.2
pH	6.1	5.9	6.2
Cd (µg/L)	n.d.	0.053	0.043
DOC (mg C/L)	5.4	6.3	4.1
Toxicity test			
H (measured, mg CaCO <sub>3</sub> /L)			
Control	1-4	5-10	5-6
H=10	not included	11-14	11-13
H=40	40-47	35-42	40-53
Mortality at zero Cd dose (%)			
Control	30	30	20
H=10	not included	15 <sup>n.s.</sup>	10 <sup>n.s.</sup>
H=40	50 <sup>n.s.</sup>	21 <sup>n.s.</sup>	5 <sup>n.s.</sup>
Reproduction at zero Cd dose (# juv./surviving parent)			
Control	48	82	50
H=10	not included	65*	58 <sup>n.s.</sup>
H=40	57 <sup>n.s.</sup>	72 <sup>n.s.</sup>	54 <sup>n.s.</sup>
NOEC (µg Cd/L)			
Control	Unreliable	2.4	5.1
H=10	Unreliable	1.8	0.95
H=40	Unreliable	<1.1	1.8
EC10 (µg Cd/L)			
Control	Unreliable	0.46 (0.08-2.6)	1.6 (0.67-3.8)
H=10	Unreliable	0.29 (0.06-1.5) <sup>n.s.</sup>	0.58 (0.27-1.3) <sup>n.s.</sup>
H=40	Unreliable	0.93 (0.5-1.7) <sup>n.s.</sup>	0.79 (0.21-2.7) <sup>n.s.</sup>
EC50 (µg Cd/L)			
Control	Unreliable	3.9 (2.3-6.1)	4.3 (2.9-6.4)
H=10	Unreliable	3.5 (2.0-6.1) <sup>n.s.</sup>	3.9 (3.0-5.2) <sup>n.s.</sup>
H=40	Unreliable	3.6 (2.8-4.6) <sup>n.s.</sup>	7.3 (4.4-12) <sup>n.s.</sup>

## Annex 2. The toxicity of Cd to *Salmo trutta* in very soft waters

(report: Study of the effect of Cd on the early life stages of brown trout *Salmo trutta* at different levels of water hardness. Haugen et al., 2007, Norwegian Institute for Water Research, report 5468-2007).

### Brief test description

The effect of water hardness on the chronic toxicity of cadmium to early life stages of brown trout has been studied in accordance with OECD Guideline 210, Fish Early Life Stage Test. The experiment consisted of a factorial design comprising three levels of hardness adjusted with CaCl<sub>2</sub> in lake Byglandsfjorden water (H=+0, +10 and +40 mg CaCO<sub>3</sub>/L) and six levels of cadmium (treatments A-F, with 0, 0.1, 0.32, 1, 3.2, 10 µg/L), including a control group of the natural background water. Eggs of brown trout were fertilised in their respective exposure water and exposed for approximately 120 days in flow-through chambers. In addition to cumulated mortality, hatching success, time-to-hatching and length and weight of larvae at four sampling points (newly fertilised eggs, eyeing stage, hatching and start feeding stage) were observed. The measured Cd concentrations were in correspondence with the nominal concentrations, with means ± SD (all treatments within Cd-groups combined, n=36) of A: 0,017 ± 0,010, B: 0,137 ± 0,035, C: 0,0313 ± 0,029, D: 0,940 ± 0,072, E: 3,041 ± 0,203 and F: 9,304 ± 0,757 µg/L). The biological effects were not very pronounced for the life stages under study. The mortality in general was very low (0.5–12%), and the high-concentration cadmium treatments were not always producing a higher mortality rate than the control. The clearest effects measured were for size- and weight at start feeding, but effects at largest Cd dose (% inhibition to control) were maximally 24%, i.e. an EC<sub>50</sub> cannot be calculated. The LOEC (measured concentration) for weight at start feeding is 0.95, 3.1 and 3.1 µg Cd/L at water hardness values of 2.7, 12.8 and 42.7 mg CaCO<sub>3</sub>/L. The statistical analysis (two way factorial with hardness and Cd levels) revealed a significant interaction term between hardness and Cd to explain weight at start feeding. This means a significant effect of hardness on Cd toxicity according to the statistical analysis in the original report. The NOEC values increased between lowest and medium hardness but not beyond that. The EC<sub>10</sub> values were estimated by a linear regression of weight (average/replicate) and log transformed measured Cd concentrations. The regression lines were significant at 0.05 levels except at the medium hardness level. The author of the report preferred to use weighed regression with a weighing factor inversely proportional to the within replicate variation (variation of individuals). With that method, all regression lines are significant at P=0.05. Both options yield a clearly different EC<sub>10</sub>. For example, the EC<sub>10</sub> at medium hardness is either 5.2 or 0.9 µg/l depending on the selection of a weighted or unweighted regression (Table A2). Other regression curves and other data analysis were tested, each yielding a different EC<sub>10</sub> value. The author of the report states that the EC<sub>10</sub> values are uncertain due to small effects found but concluded that the hardness effect is significant between the extremes. We conclude that these uncertainties should be taken forward to the conclusion. A regression of EC<sub>10</sub> (log transformed) to hardness (log transformed) yielded a hardness slope of 0.99 or 0.97 depending which EC<sub>10</sub> is chosen. Results are given in Table A2



Table A2 Summary of test results with *Salmo trutta*. Statistical tests (\*=P<0.05; n.s. P>0.05) are contrasts with control (=softest) water.

Parameter	Lake Byglandsfjorden
Lake water	
H (mg CaCO <sub>3</sub> /L)	2.7
pH	6.5
Cd (µg/L)	0.017±0.010
DOC (mg C/L)	2.0
Toxicity test	
H (measured, mg CaCO <sub>3</sub> /L)	
Control	2.7
H=10	12.8
H=40	42.7
Cumulative mortality at zero Cd dose (%)	
Control	
H=10	2.7
H=40	3.4 <sup>n.s.</sup> 4.0 <sup>n.s.</sup>
Weight at start feeding at zero Cd dose (g.)	
Control	
H=10	0.146
H=40	0.142 <sup>n.s.</sup> 0.144 <sup>n.s.</sup>
NOEC (µg Cd/L)	
Control	0.31
H=10	0.95
H=40	0.92
LOEC (µg Cd/L)	
Control	0.95
H=10	3.1
H=40	3.1
EC10 (µg Cd/L): unweighted regression	
Control	0.52
H=10	5.25
H=40	7.00
EC10 (µg Cd/L): weighted regression	
Control	0.35 <sup>a</sup>
H=10	0.91 <sup>ab</sup>
H=40	5.70 <sup>b</sup>

### Annex 3. The toxicity of Cd to *Pseudokirchneriella subcapitata* in very soft waters

(report: Effect of water hardness on the toxicity of cadmium to the alga *Pseudokirchneriella subcapitata*; Torsten Källqvist, 2007. Norwegian Institute for Water Research, Report 5422-2007.)

#### Brief test description

The growth inhibiting effect of cadmium on the green alga *Pseudokirchneriella subcapitata* has been investigated in an artificial medium and three natural soft lake waters, identical to those used for *D. longispina* test. The test followed the OECD 201 protocol. The hardness of the media was manipulated by addition of CaCl<sub>2</sub> to different levels and, in total, 17 different tests were run. Iron was supplied as FeEDTA (0.13-0.27 µM) in all media and the effect of adding or omitting this chelator was tested in 4 paired tests. The chelator reduced Cd toxicity but also reduced the variability of the endpoint, pointing to Fe-deficiency in the natural lake water. The reduction of Cd toxicity by the addition of the Fe-chelator was significant in all 4 paired tests (1 lake at 3 hardness levels and another lake at natural hardness) and the difference in toxicity at the EC10 was about a factor of 2. This means that EDTA did reduce Cd toxicity, most likely by complexing Cd in these media and, therefore, these data are not valid for the Cd risk assessment where all data using chelators in the media were not used in the aquatic risk assessment. Therefore, only data on hardness effects, observed in 1 water (Lake Sandungen) can be used. The control response in the water at the highest hardness does not strictly pass the validity criteria since the coefficient of variation (CV) of the growth rate is 9.7% whereas the protocol recommends 7% as the largest CV. However, there was no interaction between hardness level and the growth rate in the control and we propose to use these data rather than to omit all data obtained with algae. Increasing hardness resulted in a lower slope of the concentration/response curve in all media. The EC50 increased with hardness (reduced toxicity) but the effects of hardness on Cd toxicity were not significant at the EC10 levels. The lowest EC10 levels were found in the softest Lake Byglandsfjorden (hardness 3.4) in the absence of FeEDTA and the EC10 was 2.8 µg/L (2.2-3.5, 95% confidence interval). Results are shown in Table A3.

Table A3 Summary of test results with *Pseudokirchneriella subcapitata*. Confidence limits of EC10 and EC50 are given in brackets. Statistical tests (\*=P<0.05; n.s. P>0.05) are contrasts with control (=softest) water.

Parameter	Lake Sandungen
Lake water	
H (mg CaCO <sub>3</sub> /L)	6.2
pH	6.7
Cd (µg/L)	0.024
DOC (mg C/L)	4.1
Toxicity test	
H (nominal, mg CaCO <sub>3</sub> /L)	
Control	6.2
H=10	6.2+10=16.2
H=40	6.2+40=46.2
Growth rate at zero Cd dose (day <sup>-1</sup> )	
Control	1.63
H=10	1.50 <sup>n.s.</sup>
H=40	1.31 <sup>n.s.</sup>
EC10 (µg Cd/L)	
Control	7.5 (5.5-10.2)
H=10	8.5 (7.1-10.2) <sup>n.s.</sup>
H=40	6.0 (3.5-11.6) <sup>n.s.</sup>
EC50 (µg Cd/L)	
Control	29 (26-35)
H=10	41 (37-44)*
H=40	199 (158-265)*

The report provides the comprehensive risk assessment of the substance cadmium metal and cadmium oxide. It has been prepared by Belgium in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to humans and the environment, laid down in Commission Regulation (EC) No. 1488/94.

#### Part I - Environment

This part of the evaluation considers the emissions and the resulting exposure to the environment in the production of cadmium metal and cadmium oxide, the use of these substances in the production of stabilisers, pigments, alloys and plated products. Further down-stream uses are not or only limitedly included. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic and terrestrial compartment has been determined. No risk assessment was performed for the atmosphere or the marine environment. Based on newly generated ecotoxicity data under low water hardness conditions (See Addendum), no risk was identified in the soft water ranges tested. The risk remains uncertain in extremely soft waters (i.e. below 5 mg CaCO<sub>3</sub>/L).

The environmental risk assessment concludes that there is concern for the aquatic ecosystem at certain metal production, processing and NiCd batteries recycling sites. A concern for the sediment compartment is identified for the cadmium plating and alloys sector. Taken into consideration Cd bioavailability in sediments, additional risk is found at specific cadmium metal production, cadmium pigment production and cadmium recycler sites, and under specific disposal scenarios (See Addendum). For the terrestrial compartment a risk is identified at cadmium plating and alloy production sites. A borderline risk is found for soil cadmium concentrations leading to secondary poisoning. Furthermore, there is concern for micro-organisms of the wastewater treatment plants of certain NiCd battery recycling plants.

#### Part II - Human Health

This part of the evaluation is published in a separate document.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commission's committee on risk reduction strategies set up in support of Council Regulation (EEC) N. 793/93.

**European Union Risk Assessment Report**  
**CADMIUM METAL AND CADMIUM OXIDE**

CAS-No.: 7440-43-9 and 1306-19-0  
EINECS-No.: 231-152-8 and 215-146-2

**RISK ASSESSMENT**

**STAGE II: CONCLUSION (I) BIOAVAILABILITY IN SEDIMENT**

Addendum to Part I - Environment

August, 2006

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## EXPLANARY NOTE

This report is an addendum to the European Risk Assessment Report (RAR) on cadmium and cadmium oxide that has been prepared by Belgium in the context of Council Regulation (EEC) No. 793/93 on the evaluation and control of existing substances and published in 2007 on the European Chemicals Bureau Website (European Risk Assessment Report Vol.72, EUR 22919 EN)<sup>1</sup>.

In the frame of this work, the environmental risk assessment for cadmium and cadmium oxide was completed with a **conclusion (i)** for the sediment compartment. There was felt to be a need for further information regarding the bioavailability of cadmium in order to possibly refine the assessment at regional and local level. Results are presented in this report.

For detailed information on the risk assessment principles and procedures followed, the underlying data and the literature references, the reader is referred to the Risk Assessment Report.

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<sup>1</sup> European Chemicals Bureau – Existing Chemicals – <http://ecb.jrc.ec.europa.eu/>



## OVERALL RESULTS OF THE RISK ASSESSMENT - ADDENDUM

CAS Number: 7440-43-9 and 1306-19-0  
EINECS Number: 231-152-8 and 215-146-2  
IUPAC Name: cadmium metal and cadmium oxide

### Environment

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to:

- Cd plating sector and Cd alloys sector (included in the overall RAR on Cd/CdO with site-specific information dating in general from the reference year 1996) and for which no new exposure data were submitted)
- Risk is additionally identified for the benthic organisms at 4 sites and 4 disposal scenarios if the lowest regional 10<sup>th</sup> percentile (German data from 3 river systems) from the AVS database is used for the bioavailability correction instead of the 10<sup>th</sup> percentile of the entire EU AVS data which are dominated by data from NL and BE. The 4 sites and 4 scenarios are:
  - o 1 Cd metal production site, 2 Cd pigments production sites (update RAR Cd/CdO, year 2002);
  - o 1 Cd recycler (update RAR Cd/CdO year 2002);
  - o 1 MSW incineration scenario (future scenario), 3 MSW landfill scenarios.

**Conclusion (ii)** There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

This conclusion applies to:

- Cd metal/CdO production plants, Cd pigments producing plants, Cd stabiliser producing plants (that are included in the update document of the RA on Cd metal/CdO, reference year 2002; these update data and assessment overwrite the data and assessment regards the same scenarios reported in the overall RAR on Cd/CdO, reference year 1996).
- Ni-Cd battery production and recycling plants that are included in the TRAR (reference year 1999/2000).
- Present and future scenarios for local incineration plants and MSW landfill sites included in the TRAR (reference year 1999/2000).
- Ni-Cd battery production and recycling plants that are included in the update document of the RA on Cd metal/CdO (reference year 2002).
- Measured regional and continental Cd concentrations in sediments based on 90<sup>th</sup> percentiles of regional Cd data from Belgium, France, Spain, Sweden and The Netherlands.

The Cd bioavailability has been taken into account for deriving this conclusion (ii). Without such bioavailability correction, regional and local risk is predicted in some of these regions/locations.

The bioavailability correction is based on the concentration of available acid volatile sulphides (AVS) in the sediment, which reduce the toxicity in sediment (i.e. reduced risk with increasing AVS concentration). The AVS concentration is the 10<sup>th</sup> percentile of regional values (for Belgium and The Netherlands) and, for other regions and all local sites, the lowest regional 10<sup>th</sup> percentile of the EU regions (German data from 3 river systems). That 10<sup>th</sup> percentile may be revised (and conclusions as well) if other AVS data become available which is recommended given the relatively limited EU coverage of regional AVS data (only 6 countries).

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### 3.2.3 Sediment

(The text of the overall RAR version May '05 is given here with an update in revision mode).

#### Introduction

The fate of CdO powder in sediments is not documented. In the absence of this information, it is hypothesised that the metal behaves as the Cd<sup>2+</sup> salt after equilibration. Only limited relevant data on the toxicity of Cd<sup>2+</sup> to freshwater benthic organisms were found. These data refer to tests where uncontaminated sediment was spiked with Cd<sup>2+</sup> salts. Several tests with field-contaminated sediments were found. These tests cannot be used for dose-response analysis because the sediments are contaminated with various other metals and with organic compounds. Some of these tests are nevertheless included as supportive information in the review given below. Tests with marine sediments were not included for the effects assessment and PNEC derivation, however marine tests were evaluated to assess the concept that sulphide bound Cd is not toxic.

#### **3.2.3.1 Influence of sediment properties on toxicity of Cd: field validation of the AVS/SEM concept for cadmium**

There are 3 potential pathways for contaminants to reach benthic organisms: the sediment (e.g. ingestion), the overlying water and the interstitial (pore) water (e.g. across respiratory surfaces and body walls). The relative importance of each route depends on a number of factors -sediment characteristics such as type of organisms and feeding habitat (Power and Chapman, 1996).

The Cd mobility in anaerobic sediments is controlled by the concentration of acid-volatile sulphides (AVS) by the particulate organic carbon (POC) and by the dissolved organic carbon (DOC). In aerobic conditions, in which the AVS are virtually absent, Cd mobility depends on the content of the POC and of Fe and Mn-hydroxides. The toxicity of Cd most likely depends on its mobility in the sediment. Since the beginning of the 90's the role of AVS on metal toxicity in sediments has been studied intensively (Van den Berg et al., 1998, Pesch et al., 1995, Allen et al., 1993, Zhuang et al., 1994, Di Toro et al., 1992, Carlson et al., 1991). Cadmium was one of the first metals for which a relationship was found between cadmium toxicity and the AVS normalised Cd content. In general, toxicity was expected to be absent when the ratio of the simultaneously extractable metals (SEM) to the AVS < 1 (molar ratio) and could increase drastically from SEM/AVS ≥ 1. Metal toxicity above this value furthermore depend on water hardness, pH and solid phase properties. However, the molar ratio did not seem to be a good predictor of potential effects, because the ratio gives no indication about the absolute amount of SEM present in excess of AVS. Therefore, the molar difference was introduced as a better predictor. At a molar SEM-AVS difference < 0 no toxic effects are expected while at molar SEM-AVS difference > 0 toxic effects may occur.

A conclusion (i) programme (literature review) was initiated to assess if the so-called SEM/AVS theory correctly predicts no toxicity for Cd in sediments at concentrations below the AVS capacity (Vangheluwe and Versonnen 2004). The focus of that study was on toxicity, not on bioaccumulation, i.e. exceptions to the AVS concept based on uptake of Cd are not considered for the incorporation of that concept in the risk characterisation. However, some of these exceptions are discussed below.

Table 3.2.1 gives an overview of observed toxicity or absence of toxicity at  $\Sigma$ SEM/AVS below and above one in the studies described in the report of Vangheluwe and Versonnen (2004). The majority of the data confirm that toxicity due to metals is unlikely to occur at  $\Sigma$ SEM/AVS < 1.0, although one exception was found (see below). This literature includes 5 chronic studies with Cd spiked sediments. Three of the five chronic studies are marine studies. It is unknown to what extent differences between marine and freshwater environments affect the role of sulphides on Cd toxicity. The only exception to the AVS concept is based on a marine chronic study (see below) and the 2 freshwater chronic studies, which are even based on a field experiment, and the other acute freshwater studies confirm the AVS concept for Cd toxicity. The chronic studies are also summarised in Fig. 3.2.1. Details of these studies are given in Appendix 2 of this document.

One exception to the SEM/AVS concept was found in a chronic colonisation test with a Cd spiked marine sediment containing relatively high AVS concentrations (Hansen et al., 1996): no toxicity was evident at about 170 mg Cd/kg ( $\Sigma$ SEM/AVS=0.3) whereas incipient toxicity was found at about 1360 mg Cd/kg ( $\Sigma$ SEM/AVS=0.79), i.e. at SEM/AVS < 1.0. The ratio of 0.79 refers to a homogenised sediment sample (0-8 cm) whereas the ratio SEM/AVS was >1 in the upper 2.4 cm upper layer due to oxidation. The authors of that study concluded that the SEM/AVS concept remains valid provided that the vertical heterogeneity is accounted for. Current AVS data of the EU refer to sediments collected by a grab sampler. With this device the sampling depth is, on average, 10 cm with a maximum depth of 20 cm (personal communication with Ward De Cooman, VMM, 26-01-05). The AVS concentrations are larger at larger depth. This means that, on the one hand, the current AVS data for EU somewhat overestimate the AVS of the surface layers. On the other hand, the total metal concentrations used for the PEC derivations also often originate from monitoring studies conducted with grab samplers and reflecting the metal contamination over a larger depth (including historical contamination).

Ankley (1996) did a comprehensive review of studies on Cd *bioaccumulation* (not toxicity) and concluded that the preponderance of these studies indicated reduced accumulation of metals at sediment metal/AVS ratios of less than 1. Nevertheless, bioaccumulation was observed at ratios of SEM/AVS < 1 in some of the studies reviewed and which is confirmed by more recent studies (Lee et al 2000a, 2000b; Griscom et al. 2000; Otero et al. 2000; Lee et al. 2001; Griscom et al. 2002). Lee et al. (2000a) did not find a correlation between metal concentrations in animal tissue of four benthic organisms and metal concentrations in pore water. The metal concentrations in the animal tissue were correlated with the metal concentrations extracted from the sediment, indicating that exposure of these organisms principally occurred through ingestion of particles. Therefore, the AVS-based approach may be appropriate for protecting some, but not all, benthic organisms. These results question the notion that metal bioavailability in sediments is controlled only by geochemical equilibration of metals between pore water and reactive sulphides and indicates that feeding behaviour and dietary uptake next to pore water may play a role in the bioaccumulation of metals. It should be kept in mind that bioaccumulation does not represent a toxicological effect and an unambiguous connection between observed levels of accumulation and effects has not yet been made.

To conclude, the weight of evidence correctly predicts the absence of *toxicity* of Cd in several studies, including acute, chronic and field recolonisation studies, where excess AVS was present. **We therefore propose to use the sediment AVS concentration as a factor controlling the Cd toxicity in sediments.** Exceptionally, toxicity was observed in a laboratory experiment while according to the SEM/AVS model Cd should not be bioavailable, but this was explained by SEM/AVS ratio above 1 in the upper sediment layer. This points, however, to a major drawback of the SEM/AVS concept, i.e. the variability of SEM/AVS with sediment depth and a lack of

guidance on the sediment sampling depth for SEM/AVS analysis. The exception to the AVS concept was found at very large AVS and large total Cd concentration (LOEC: 1360 mg Cd/kg, i.e. >100-fold above regional sediment concentration). It is logical that small spatial or temporal variation in AVS can have a larger impact on Cd toxicity at these large concentrations, suggesting that the SEM/AVS concept should be adopted in a conservative way by also considering the absolute concentration. The proposal to include conservatism is that the 10<sup>th</sup> percentile of available AVS will be used for the regional risk characterisation rather than the 50<sup>th</sup> percentile of available AVS to correct for bioavailability. It will be shown that the choice of the 10<sup>th</sup> percentile of AVS as the regional value for correcting for bioavailability will reveal risk at a total sediment Cd concentrations that is well below the NOEC/LOEC value of the only study where the exception was found. For a local risk characterisation, where measured data may become available, it is recommended to sample the surface layer of the sediment.

**Table 3.2.1 Overview of observed toxicity or absence of toxicity in relation to SEM/AVS in the studies described by Vangheluwe and Versonnen (2004). Sediments can be from marine (M) or freshwater (F) origin. All chronic studies are Cd spiked sediments and the SEM&AVS data refer to homogenised samples of the sediment. The SEM values of chronic studies include all metals (Cd, Ni, Zn, Cu and Pb) except for the study of De Witt et al., 1996.**

Author	Type of test	M/F	Species	AVS(μmol/g)	Toxic effects observed at		NOEC/LOEC (mg Cd/kg <sub>dw</sub> )
					SEM/AVS < 1	SEM/AVS > 1	
Di Toro et al., 1990	Acute	M	<i>Ampelisca abdita</i> <i>Rhepoxynius hudsoni</i>		no	yes	
Carlson et al., 1991	Acute	F	<i>Lumbriculus variegatus</i> <i>Helisoma sp</i>		no <sup>(a)</sup>	yes	
Pesch et al., 1995	Acute	M	<i>Neanthes arenaceodentata</i>		no	no + yes	
Berry et al., 1996	acute	M	<i>Ampelisca abdita</i>		no	no + yes	
Höss et al., 2001	acute	F	<i>Caenorhabditis elegans</i>		no	yes	
De Witt et al., 1996	chronic	M	<i>Leptocheirus plumulosus</i>	19.3	no	no + yes	1370/1950
Hare et al., 1994	chronic: field recolonisation	F		0.5	no	no+yes	115/560
Hansen et al., 1996	chronic laboratory recolonisation	M		17.2	no + yes <sup>(b)</sup>	yes	168/1360
Boothman et al., 2001	chronic: field recolonisation	M		9.0	no	no	>600
Hare et al., 2001	chronic: field recolonisation	F		0.8-2.8		no+yes <sup>(c)</sup>	180/315

<sup>(a)</sup> LC<sub>50</sub> for *L. variegatus* = 1 μmol total Cd/μmol AVS; <sup>(b)</sup>SEM/AVS exceeded 1 in the upper sediment but not in the homogenised sediment sample; <sup>(c)</sup> no 'overall' toxicity up to highest concentration tested according to authors, however 2 species are affected at highest dose.

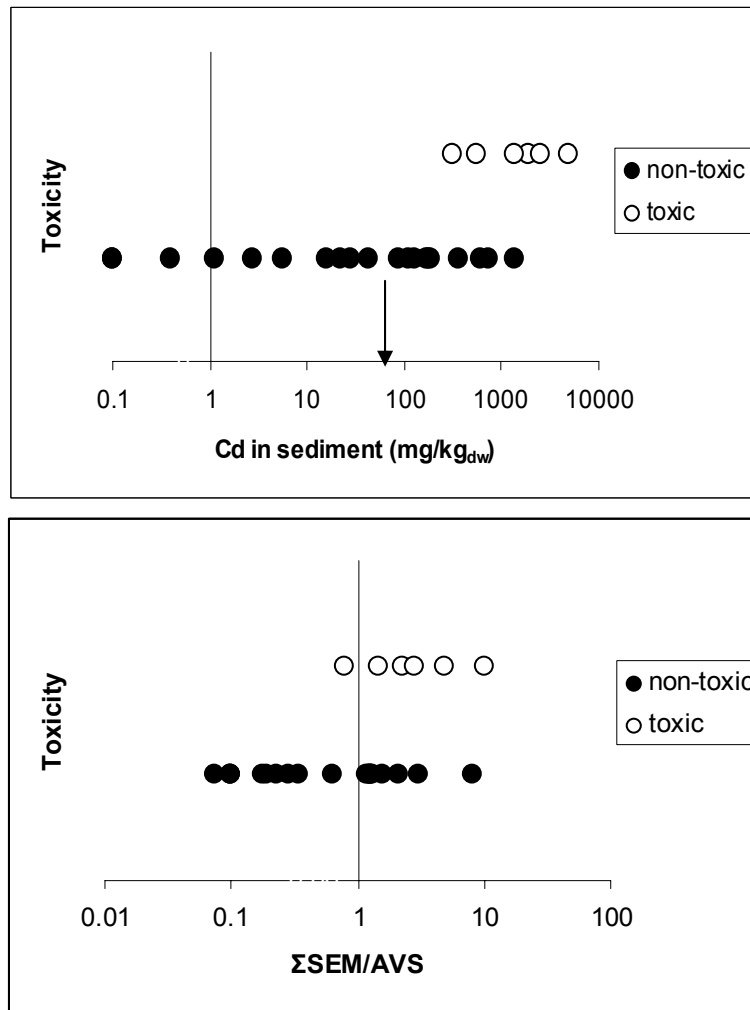


Fig. 3.2.1. Chronic toxicity in Cd spiked sediments, each point representing a different concentration of each test. The SEM&AVS data refer to homogenised samples The point where toxicity is found at  $\Sigma\text{SEM}/\text{AVS} < 1$  refers to a study where SEM also includes Ni, Pb, Zn and Cu. Arrow in top graph illustrates where regional risk is predicted assuming a generic value for available AVS (see text).



### 3.2.3.2 Acute and prolonged toxicity to benthic organisms

**Table 3.2.2: selected data with RI 1-3 for Cd toxicity to benthic organisms. Eighteen tests were reviewed from 6 source documents and 15 tests were selected.**

	min	median	max	n
NOEC (mg kg <sub>dw</sub> <sup>-1</sup> )	115	680	3390	16
LOEC (mg kg <sub>dw</sub> <sup>-1</sup> )	315	334	1079	3
E(L)C <sub>x&gt;50</sub> (mg kg <sub>dw</sub> <sup>-1</sup> )	563	1400	6200	13

A summary of the literature review is given in Table 3.2.2. The Cd concentrations in the sediment/water systems are either expressed per unit sediment dry weight ( $\mu\text{g g}^{-1}_{\text{dw}}$ ) or as the dissolved fraction in the liquid phase ( $\mu\text{g L}^{-1}$ ). The main factors influencing toxicity results are physico-chemical characteristics of the test medium, test species (physiological behaviour), life stage of the test organisms, test design and preparation of the test medium. The criteria for defining reliability indices are explained for each source document in the IUCLID document. Data obtained from mixed polluted sediments were considered unreliable (RI 4).

Carlson et al. (1991) and Di Toro et al. (1992) studied the influence of the type of sediment on toxicity of Cd. Carlson et al. (1991) tested Cd toxicity to *Lumbricus variegatus* in two lake sediments and one river sediment. The sediments were contaminated with Cd ( $40\text{-}16000 \mu\text{g g}^{-1}_{\text{dw}}$ ) by equilibrating the sediment with Cd spiked Lake Superior water. The LC<sub>50</sub> values varied from  $700\text{-}6000 \mu\text{g g}^{-1}_{\text{dw}}$ . The LC<sub>50</sub> values were positively related with the AVS—content, i.e. more AVS reduces Cd toxicity.. Similar dose-response curves were obtained for the three sediments if the sediment Cd concentration was normalised per unit AVS. Cadmium was extracted with cold hydrochloric acid ([Cd]<sub>SE</sub>), simultaneous with AVS. No toxicity was recorded when [Cd]<sub>SE</sub>/AVS<1 (molar concentration ratio). Mortality increased sharply to 100% when [Cd]<sub>SE</sub>/AVS≥1. Di Toro et al. (1992) performed similar tests with the same test species and sediments of the same three locations. They found no unique relationship between [Cd]<sub>SE</sub> (mg kg<sup>-1</sup><sub>dw</sub>) and mortality of the test organisms for the different freshwater sediments. By contrast, a clear mortality-concentration relationship was observed when relating mortality to the [Cd]<sub>SE</sub>/AVS molar ratio. No mortality in excess of 20% was observed for sediments with [Cd]<sub>SE</sub>/AVS<1. For sediments with [Cd]<sub>SE</sub>/AVS>1-3, mortality increased significantly. Similar results were found by Hansen et al (1996a) for mixed polluted sediments. The simultaneously extractable metals (SEM) however included Cd+Cu+Ni+Zn+Pb. The authors conclude that the AVS is a reactive pool that binds heavy metals and render them unavailable to biota. Hare et al. (1994) studied the in situ colonisation of Cd-spiked freshwater sediments by macroinvertebrates in a chronic field study. Lake sediments below the top 10 cm layer was sampled, spiked with Cd, transferred to 8-L test trays and then installed in the lake bottom at 15 m depth. The mean total abundance for all taxa in the test trays was not significantly related to Cd exposure. Taken individually (at species level), the abundances of most species also did not appear to be related to exposure up to the highest Cd exposure level ( $563 \mu\text{g Cd g}^{-1}_{\text{dw}}$ ). Only the number of *Chironomus (salinarius) sp.*, which is one of the most abundant *Chironomidae* species, was strongly reduced at  $563 \mu\text{g Cd g}^{-1}_{\text{dw}}$ . Larvae of this species burrow deep in the sediment and have their guts filled with sediment, indicating a high exposure via sediment intake.

The physiological behaviour of the test species affects their sensitivity to Cd. Carlson et al. (1991), Di Toro et al. (1992) and Francis et al. (1984). Mortality of the worm *Lumbricus variegatus* and the snail *Helisoma* sp. was measured in spiked sediments (Carlson et al. 1991, Di Toro et al. 1992). *Lumbricus* was found to be the most sensitive to Cd in 4 out of the 6 different freshwater sediments. The higher sensitivity of the worms was attributed to the extended exposure of the worms due their life strategy. *Lumbricus* is usually half buried in the sediment while the other half remains in the overlying water for respiration. The snails however remain on the surface of the sediment, decreasing their contact with Cd in the sediment. Francis et al. (1984) investigated the effect of Cd-enriched sediment on goldfish, leopard frog and largemouth bass in the embryonic and larvae stages. The sediment was contaminated between 1 and 1000 mg kg<sup>-1</sup><sub>dw</sub>. No effects on survival were found up to the highest level for goldfish and frog. There was, however, 14 % mortality at hatching of the bass larvae at the highest Cd level. The authors attribute the higher sensitivity of bass to the extended contact time of embryos and larvae with the contaminated sediment. Eggs of largemouth bass are settled onto the sediment and larvae remain there after hatching. Embryos and larvae of goldfish and leopard frog however remain in the overlying water and are less exposed to Cd in the sediment.

Nebeker et al. (1986b) studied survival of *Hyaella azteca* in Cd-spiked water and in sediment. Tests were performed in static and flow through conditions. The Cd concentrations in the solutions of the flow through systems were far below those in the static system. In the flow-through test, Cd had no effect on mortality of *Hyaella azteca* whereas in the static test, effects are found in sediment/water systems containing 20 µg Cd L<sup>-1</sup>. The gradient between the pore water and bottom water Cd concentrations is disturbed in flow-through systems. Therefore the pore water and bottom water concentrations decrease and the sediment appears to be less toxic.

**Table 3.2.3: Toxicity to benthic organisms. All underlined data are selected for the effect assessment**

test substance	organism	medium	test conditions	Nominal/Measured	Equilibration period (d)	Duration (d)	endpoint	NOEC		Cat*	LOEC		EC <sub>x250</sub>		references	R.I.
								µg g <sup>-1</sup> dw	µg L <sup>-1</sup>		µg g <sup>-1</sup> dw	µg L <sup>-1</sup>	µg g <sup>-1</sup> dw	µg L <sup>-1</sup>		
CdCl <sub>2</sub>	<i>Helisoma sp.</i>	uncontaminated freshwater sediment from: Pequawan Lake East River West Bearskin Lake	semi-static; sed./water:1:3 (vol)  AVS: 42 µmol/g AVS: 8.8 µmol/g AVS: 3.6 µmol/g	M-total	/	10	mortality	<u>3390</u>	1					<u>4520</u>	Di Toro et al., 1992	3
								<u>2260</u>	1					<u>3340</u>		
								<u>340</u>	1					<u>790</u>		
	<u>3390</u>							1	<u>4520</u>							
	<u>680</u>							1	<u>1130</u>							
	<u>340</u>							1	<u>680</u>							
CdCl <sub>2</sub>	<i>Hyalella azteca</i>	natural sediment (Soap Creek Pond - Oregon State University); 200 ml spiked natural sediment + 800 ml well water	static; T 19°C; sediment characteristics: 3% organic carbon, 15% sand, 29% silt, 56% clay; water characteristics: pH 7.1, H 54 mg L <sup>-1</sup> CaCO <sub>3</sub> , BC < 0.5 µg L <sup>-1</sup> . AVS unknown	M (diss.)	0.5	4	mortality	<u>167</u>	1.1	2	<u>334(26)</u>	3.2		6.6	Nebeker et al., 1986b	3
CdCl <sub>2</sub>	<i>Micropterus salmoides</i>	natural stream sediment; 250 g <sub>dw</sub> sediment + 25 ml Cd-solution or distilled deionized water (control) +350 ml reconstituted water	DO 6.6-8.1 mg L <sup>-1</sup> , T 22.1-22.5 °C, pH 7.9-8.4; sed: OM 2.3%, Cd <sub>T</sub> 1.02 mg kg <sup>-1</sup> , Zn <sub>T</sub> 108.2 mg kg <sup>-1</sup> , Fe <sub>T</sub> 5.52%; 5.52% sand, 35.4% silt, 12% clay	M	0.42	7	mortality	<u>540</u>	22	2	<u>1079 (14)</u>	44 (14)			Francis et al., 1984	3
CdNO <sub>2</sub>	<i>Chironomus (salinarius) gp) sp.</i>	natural lake sediment (Lake Tantaré, Canada), sampled below the top 1-10 cm; spiked sediments in test trays replaced in the test location in the lake	field test; water characteristics: pH 5.5-5.6, H 3; sediment characteristics: AVS: 0.5 µmol/g <sub>dw</sub>	N	/	14 months	abundance	<u>115</u>		1			<u>563 (80)</u>		Hare et al., 1994	2
CdCl <sub>2</sub>	<i>Lumbricus variegatus</i>	Pequawan Lake East River sediment West Bearskin Lake	sediment AVS content: 38-32 µmol/g 6.8-7.3 µmol/g 2.8-3.2 µmol/g	M	4	10	mortality	<u>3000</u>						<u>6000</u>	Carlson et al., 1991	2
								<u>800</u>	1					<u>1400</u>		
								<u>380</u>	1					<u>700</u>		
	<u>3000</u>								<u>6200</u>							
	<u>2300</u>							1	<u>4100</u>							
	<u>2300</u>							1	<u>4100</u>							

test substance	organism	medium	test conditions	Nominal/ Measured	Equilibration period (d)	Duration (d)	endpoint	NOEC		Cat*	LOEC		EC <sub>50</sub>		references	R.I.
								µg g <sup>-1</sup> <sub>dw</sub>	µg L <sup>-1</sup>		µg g <sup>-1</sup> <sub>dw</sub>	µg L <sup>-1</sup>	µg g <sup>-1</sup> <sub>dw</sub>	µg L <sup>-1</sup>		
			test water: sand filtered Lake Superior water; T 21-22 °C, alkalinity 45-46 mg L <sup>-1</sup> , hardness 44-45 mg L <sup>-1</sup> , pH 7.9-8, dissolved oxygen concentration >6 mg L <sup>-1</sup> , continuous flow; T 23°C; 1.5L Cd sol. + 1L sed.					380		1			810			
Cd <sup>2+</sup> salt	Field recolonisation Most sensitive species: Polypedilum sp. and tubificid oligochaetes	natural lake sediment (Lake Laflamme Canada), sampled below the top 10 cm; spiked sediments in test trays replaced in the test location in the lake	Pore water: pH 6.5, 30 µM sulphate. AVS: 0.8-2.8 µmol/g	M	11 months	11 months	abundance	180			315				Hare et al., 2001	3
<b>Supporting data</b>																
CdCl <sub>2</sub>	<i>Hyalella azteca</i>	contaminated freshwater sediment from Foundry cove	semi-static; sed./water:1:3 (vol) AVS: 0.1-47 µmol/g; SEM (Ni+Cd) 0.3-1000 µmol/g	M-total	/		mortality						17 (100)		Di Toro et al., 1992	4
CdCl <sub>2</sub>	<i>Rana pipiens</i> <i>Carassius auratus</i>	natural stream sediment; 250 g <sub>dw</sub> sediment + 25 ml Cd-solution or distilled deionized water (control) +350 ml reconstituted water	DO 6.6-8.1 mg L <sup>-1</sup> , T 22.1-22.5 °C, pH 7.9-8.4; sed: OM 2.3%, Cd <sub>T</sub> 1.02 mg kg <sup>-1</sup> , Zn <sub>T</sub> 108.2 mg kg <sup>-1</sup> , Fe <sub>T</sub> 5.52%; 5.52% sand, 35.4% silt, 12% clay	M	0.42	7	mortality	1074(H T)	77						Francis et al., 1984	4 4
Cd <sup>2+</sup>	<i>Hyalella azteca</i>	natural sediment: Foundry cove	% total organic carbon: 0.55-16.4 µg/g, total Cd: 0.4-38900 µg/g, total Cu: 18-143 µg/g, total Ni: 18-31500 µg/g, total Pb: 6.1-357 µg/g, total Zn: 65-403 µg/g, sum metals: 2.9-893, SEM: 0.2-779 µmol/g, AVS: 0.4-64.6 µmol/g, SEM/AVS: 0.02-139	M-total	/	10	mortality	72			363(20)				Hansen et al., 1996a	4

TOC: total organic carbon; AVS: acid volatile sulphides; H: water hardness (mg CaCO<sub>3</sub> L<sup>-1</sup>); \*NOEC classification (see section 3.2.0.2)

### 3.2.3.3 The PNEC<sub>sediment</sub> derived without correction for bioavailability

There are 2 sediment toxicity tests available within the data set that can be considered as chronic tests (test duration of other tests are 4-10 days and use mortality as endpoint). The statistical extrapolation technique will therefore not be used on the NOEC data and two alternative methods will be proposed.

According to the TGD (TGD 1996, p.335), the PNEC<sub>sediment</sub> may be calculated using the equilibrium partitioning (EP) method in the absence of ecotoxicological data for sediment-dwelling organisms. Based on the equilibrium partitioning, the following formula is applied to calculate PNEC<sub>sediment</sub> (mg kg<sup>-1</sup><sub>ww</sub>):

$$PNEC_{\text{sediment}} = \frac{K_{\text{sed-water}}}{RHO_{\text{sediment}}} \cdot PNEC_{\text{water}} \cdot 1000$$

with PNEC<sub>water</sub> expressed in mg L<sup>-1</sup>, RHO<sub>sediment</sub> the bulk density of wet sediment (kg ww m<sup>-3</sup>), K<sub>sed-water</sub> the water-sediment partition coefficient (m<sup>3</sup> m<sup>-3</sup>).

This equation can be transformed to a dry weight based PNEC<sub>sediment</sub> as

$$PNEC_{\text{sediment}} = K_p \cdot PNEC_{\text{water}} \cdot 10^{-3}$$

in which K<sub>p</sub> equals the solid-water partition coefficient of suspended matter, expressed in L kg<sup>-1</sup>, and PNEC<sub>water</sub> expressed in µg L<sup>-1</sup>. This transformation has assumed that the fraction Cd in the pore water can be neglected compared to the total amount of Cd in the sediment. Even at the lowest K<sub>p</sub> assumed in the Table below, this fraction is less than 0.01%. The PNEC<sub>water</sub> equals 0.19 µg L<sup>-1</sup> (section 3.2.1.7 of the overall RAR on Cd/CdO). The K<sub>p</sub> ranges 17 10<sup>3</sup> L kg<sup>-1</sup>- 224 10<sup>3</sup> L kg<sup>-1</sup> (typical value , 130 10<sup>3</sup> L kg<sup>-1</sup> see 3.1.2.3.1, Table 3.1.4 of the overall RAR on Cd/CdO). The TGD stipulates an upper limit of K<sub>p</sub> beyond which an additional safety factor of 10 should be included (either in PNEC or in PEC) to take the risk of direct ingestion into account. This upper limit is at K<sub>p</sub> of about 2000 L kg<sup>-1</sup>. This situation is certainly the case for Cd, therefore the PNEC should be lowered by a factor of 10 in all cases, i.e. the PNEC<sub>sediment</sub> should be calculated in this case as

$$PNEC_{\text{sediment}} = K_p \cdot PNEC_{\text{water}} \cdot 10^{-4}$$

This results in:

K <sub>p</sub> (L kg <sup>-1</sup> )	PNEC <sub>sediment</sub> (mg Cd kg <sup>-1</sup> <sub>dw</sub> )
17000	0.32
130000	2.5
224000	4.3

The ‘generic’ PNEC<sub>sediment</sub> derived with the EP method using the typical K<sub>p</sub> values of suspended matter is, therefore, 2.5 mg Cd kg<sup>-1</sup><sub>dw</sub>

Another approach to calculate the PNEC<sub>sediment</sub> is using the assessment factor (AF) method. The lowest NOEC of the chronic tests (115 mg kg<sup>-1</sup>) is divided by an AF of 50. The choice of an AF of 50 instead of 100 is justified by the number of acute toxicity data, showing no differences between species. This results in

$$PNEC_{\text{sediment}} = 115 \text{ mg kg}^{-1} / 50 = 2.3 \text{ mg Cd kg}^{-1}_{\text{dw}}$$

The AF method yields a PNEC that is almost identical as the 'generic' PNEC<sub>sediment</sub> derived with the EP method. The AF method however predicts a PNEC which is even below the background value of the sediment in which the lowest chronic NOEC was found (2.8 mg Cd kg<sup>-1</sup><sub>dw</sub>, Hare et al., 1994). The separation between the PNEC and effect concentrations (n=15) is higher than 100-fold, and this is large for natural elements. Additional chronic toxicity data (currently not found) could remove this concern by reducing the AF to 10 or below. However, it should be recalled that sediment toxicity tests spiked with Cd have little field relevance because Cd availability can remain low as long as the capacity of free sulphides (AVS) in the sediment is not exceeded. Mixed metal pollution is the rule rather than the exception in the field and the Cd availability in a metal polluted sediment is larger than in a clean sediment. The AVS normalisation method proposed by DiToro et al. (2000) for predicting chronic effects can be a useful alternative.

The rapporteur of the present document has clear reservations against the AF method (see above) but has no other choice than selecting the AF above the EP method for a pragmatical reason: the EP method that includes the safety factor 10 leads to an enigma that risk is predicted in all local scenario's, even if emissions are zero and the Cd concentrations in water are within the *natural* background range. This enigma remains whatever the choice of K<sub>p</sub> as will be demonstrated in the next paragraph.

The local risk characterisation method of the TGD uses the risk factor for sediment, defined as  $PEC_{local, sed} / PNEC_{sediment}$ . The  $PEC_{local, sed}$  is calculated from the local water concentrations and the suspended matter-water partitioning coefficient (Eqn. 35 in the TGD). It can be shown that  $PEC_{local, sed} / PNEC_{sediment}$  effectively eliminates the K<sub>p</sub> factor in the nominator and denominator, leading to  $PEC_{local, sed} / PNEC_{sediment} = 10 * PEC_{local, water} / PNEC_{water}$ . In simple terms, this means that the risk is predicted (risk factor above 1.0) when the local water concentration is larger than the  $PNEC_{water} / 10$ , i.e. risk for the sediment compartments is predicted when the Cd concentration in the overlying water is above 0.019 µg L<sup>-1</sup>. The natural background Cd concentration is estimated as 0.050 µg Cd L<sup>-1</sup> (section 3.1.2.4.3) which means that risk is predicted even when emissions are zero and where the Cd concentrations in water are background. Different hypothesis can be forwarded to explain this enigma (i) the benthic organisms may be less sensitive to Cd than aquatic organisms; (ii) exposure via the pore water is the dominant route and the safety factor 10 is overly protective; (iii) the Cd concentrations in the pore water of sediment are lower than that in the overlying water in contrast with the TGD method that assumes equal concentrations in local scenarios; formation of metal sulphides that reduce Cd<sup>2+</sup> activity in sediments compared to the overlying water can explain such reductions. The safety factor 10 could be disregarded to avoid the enigma with the EP method, however no consensus was reached at the Technical Meetings.

### **3.2.3.4 The implementation of the AVS theory for the risk assessment of Cd in sediments at the regional scale**

#### **3.2.3.4.1 The effects assessment: calculation of PNEC<sub>sediment,available</sub>**

The risk assessment of Cd in sediments should only address the 'available Cd', i.e. the excess Cd above the 'available AVS', formally total Cd minus available AVS, both values in µmol/g. The 'available' AVS is the total AVS corrected for the amount already used to precipitate Cu and Pb because these metal sulphides are less soluble than Cd (see below). This 'available Cd'

concentration should be contrasted to the  $PNEC_{\text{sediment}}$  similarly expressed as ‘available Cd’ or, formally:

$$\text{Risk} = \frac{PEC_{\text{sediment,available}}}{PNEC_{\text{sediment,available}}} = (PEC_{\text{sediment-available AVS}}) / PNEC_{\text{sediment,available}}$$

The  $PNEC_{\text{sediment,available}}$  is different from the one derived in the preceding paragraph because that  $PNEC$  was based on a sediment containing AVS, hence containing also a non-bioavailable fraction. There are only 2 sediment toxicity tests available within the data set that can be considered as chronic tests (test duration of other tests are 4-10 days and use mortality as endpoint). The statistical extrapolation technique will therefore not be used on the NOEC data. The  $PNEC_{\text{sediment,available}}$  is, therefore, derived using the assessment factor (AF) method on the lowest NOEC value, expressed as ‘available Cd’, i.e. the total Cd NOEC minus available AVS, both expressed in molar units..

The NOEC from the study of Hare et al. (1994) is 115 mg/kg<sub>dw</sub> or 1.02 μmol/g<sub>dw</sub>, and the ‘available’ AVS in the sediments of that study is 0.37 μmol/g<sub>dw</sub> (AVS=0.5 μmol/g<sub>dw</sub> and Pb+Cu=0.13 μmol/g<sub>dw</sub>). The ‘available’ NOEC is, hence, 1.02-0.37= 0.67 μmol/g. The NOEC from the study of Hare et al. (2001) is 180 mg/kg<sub>dw</sub> or 1.60 μmol/g<sub>dw</sub>, and the ‘available’ AVS in the sediment of s that study is estimated about 0.87 μmol/g<sub>dw</sub> (AVS=1.05 μmol/g<sub>dw</sub>, ΣSEM=1.07 μmol/g<sub>dw</sub> in the control and SEM<sub>Zn</sub>=0.89 μmol/g<sub>dw</sub>; assuming minor contribution of Ni, it is estimated that SEM<sub>Cu+Pb</sub> is 1.07-0.89=0.18; the ‘available’ AVS is, therefore, 1.05-0.18=0.87 μmol/g<sub>dw</sub>). The ‘available’ NOEC is, hence, 1.60-0.87= 0.73 μmol/g<sub>dw</sub>.

The lowest NOEC, expressed as ‘available Cd’, is 0.67 μmol/g (Hare et al., 1994). This value is divided by an AF of 50. The choice of an AF of 50 instead of 100 is justified by the number of acute toxicity data, showing no differences between species, yielding

$$PNEC_{\text{sediment,available}} = 0.67/50 = 0.013 \mu\text{mol Cd/g}_{\text{dw}} (= 1.5 \text{ mg Cd/kg}_{\text{dw}}).$$

#### 3.2.3.4.2 The exposure assessment: calculation of the $PEC_{\text{sediment,available}}$

For regional risk characterisation, there are almost no data available where AVS and SEM values are coupled. In applying the SEM/AVS concept for Cd, it has to be taken into consideration that ΣSEM represents the sum of different metals acting in a competitive manner when binding to AVS. Cadmium is one of the metals which have a high affinity for binding with sulfides present in the sediment. Acknowledging the existence of competitive displacement kinetics between various metals and reduced sulfur, the SEM-AVS model can be made cadmium specific. The procedure that is used is to assign the AVS pool to the metals in the sequence of their sulfide solubility products. Ranked from the lowest to the highest solubility product the following sequence is observed: SEM<sub>Cu</sub>, SEM<sub>Pb</sub>, SEM<sub>Cd</sub>, SEM<sub>Zn</sub> and SEM<sub>Ni</sub>. Meaning copper has the highest affinity for AVS, followed by lead, cadmium etc until the AVS is exhausted. In the case of cadmium, the available Cd can be calculated as follows:

$$PEC_{\text{sediment,available}} = \text{available Cd} = PEC_{\text{sediment}} - (AVS_{\text{tot}} - \Delta AVS_{\text{Cd}})$$

with  $\Delta AVS_{\text{Cd}}$  = available AVS as:

$$\Delta AVS_{\text{Cd}} = AVS_{\text{tot}} - SEM_{\text{Cu}} - SEM_{\text{Pb}}$$

with all values in μmol/g<sub>dw</sub>. Mercury binds stronger to sulphides than Cd and should also be subtracted from the AVS pool, however paired/coupled Hg sediment monitoring data are

generally lacking. The Swedish monitoring database shows that the Hg/Cd molar ratio in sediments is usually 0.25 to 0.05 (Parkman, personal communication).

We propose to use the regional 90<sup>th</sup> percentiles of measured Cd values for Cd in sediment and to use a *corresponding* value of the 10<sup>th</sup> percentile of  $\Delta AVS_{Cd}$  ( $=AVS_{total} - SEM_{Cu} - SEM_{Pb}$ ) from to estimate the available Cd at the regional scale, i.e.

$$PEC_{\text{regional,available}} = PEC_{\text{regional,measured}} - 10^{\text{th}} \text{perc.}(\Delta AVS_{Cd}) \text{ (all values in } \mu\text{mol/g)}.$$

A generic risk assessment uses ‘typical’ (e.g. median’ values for abiotic factors controlling exposure). However, since there is concern that the  $\Delta AVS_{Cd}$  is overestimating the AVS in the biological active surface layer (see 3.2.3.1), we propose to use the 10<sup>th</sup> percentile as a conservative estimate. The value of the 10<sup>th</sup> percentile of  $\Delta AVS_{Cd}$  has a large impact on the risk characterisation and this will be exemplified with some data below.

The information of  $\Delta AVS_{Cd}$  data is very limited at a regional scale. Recently, a compilation of existing SEM/AVS databases in Europe was made. Based on this compiled SEM/AVS database (data from Belgium, The Netherlands, Italy, Germany, Sweden and the UK), a probabilistic model for the regional assessment of bioavailable Cd in the sediment compartment was developed (Vangheluwe et al., 2004, see also annex 2 of this document). Frequency distributions of ambient total AVS and  $SEM_{Cd}$  exposure concentrations in the sediments were estimated in order to derive the predicted environmental concentration (PEC) for the sediment compartment. Based on the overall freshwater data set available for Europe a median AVS concentration of 8.1  $\mu\text{mol/g}_{dw}$  and 10<sup>th</sup>-90<sup>th</sup> percentiles of 0.79-75.5  $\mu\text{mol/g}_{dw}$  was calculated. For the Flemish database of coupled measured data the probability of obtaining bioavailable Cd (i.e.  $SEM_{Cd} - \Delta AVS_{Cd} > 0$  or  $SEM_{Cd}/\Delta AVS_{Cd} > 1$ , with  $\Delta AVS_{Cd} = AVS_{tot} - SEM_{Cu} - SEM_{Pb}$ ) was 2.1 %, i.e. the probability that no available  $SEM_{Cd}$  is present, and consequently, no toxicity is predicted in sediments, is 97.9 %. Based on a Monte Carlo analysis on the aggregated dataset for Europe the probability of observing bioavailable Cd was 3.3 %. Furthermore, frequency plots showed that combinations of very low AVS and very high  $SEM_{Cd}$  are seldom found in the real environment.

A best fit analysis has been performed on the coupled SEM-AVS data from Europe (n=226) to derive the  $\Delta AVS_{Cd}$  values (Figure 3.2.2). The estimated 10<sup>th</sup> percentile is 0.49  $\mu\text{mol/g}_{dw}$  and a median value of 8.06  $\mu\text{mol/g}_{dw}$ .



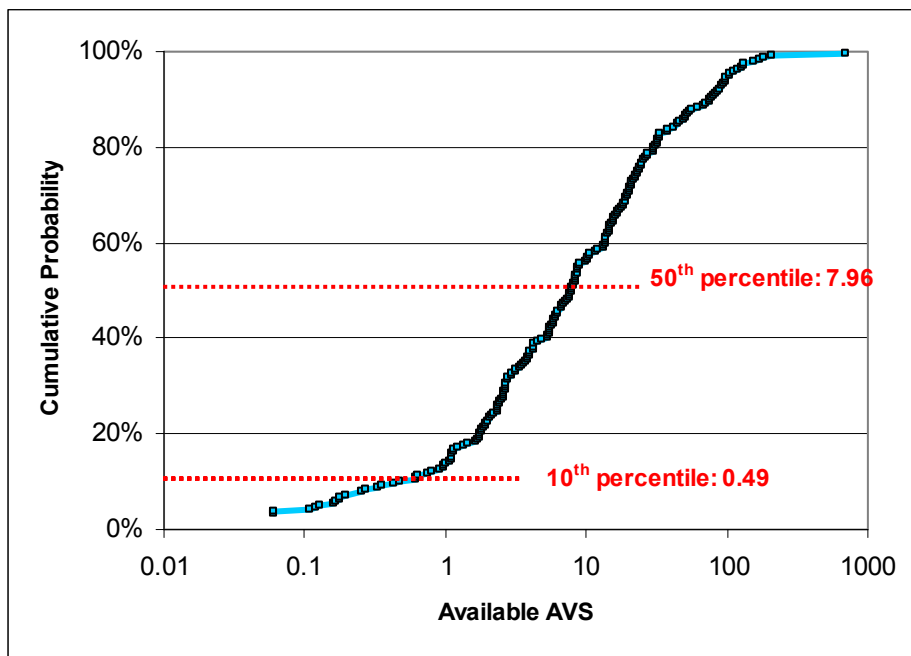


Figure 3.2.2: cumulative distribution function of  $\Delta AVS_{Cd}$  values

The EU AVS database is dominated by data from Flanders where the samples were taken in the spring. It can be expected that the AVS levels measured during a winter/spring sampling campaign represent a worst case scenario (i.e. lowest AVS levels). The 10<sup>th</sup> percentile of the AVS is generally referring to typical ‘oxic’ sediment: Redox measurements were not made in the Flemish database (n=200) but the observations in the field protocols (available for 150 of the 200 sediments) were used as a rough allocation tool to distinguish between oxic (brown color) and anoxic (gray/black color) conditions. As such the database was split in oxic and anoxic sediments. This exercise yields a median AVS value of 2.27  $\mu\text{molAVS/g}_{dw}$  for the sediments with a brown color. All sediments in the Flemish data set for which no color was available with an AVS concentration lower than this value were subsequently considered oxic. The median value of all oxic sediments (43 sediments in total) is 0.82  $\mu\text{mol AVS/g}_{dw}$ . This value confirms that the 10<sup>th</sup> percentile of  $\Delta AVS_{Cd}$  (i.e. 0.49  $\mu\text{mol/g}_{dw}$ ) is generally referring to ‘oxic’ sediments.

Figure 3.2.3 gives an overview of the  $\Delta AVS_{Cd}$  for other regions for which data are available. Figure 3.2.4 gives detailed overview of the left tail of the distribution. The red line represents the 10<sup>th</sup> percentile of the  $\Delta AVS_{Cd}$  distribution for Flanders (0.54  $\mu\text{mol/g}_{dw}$ ).

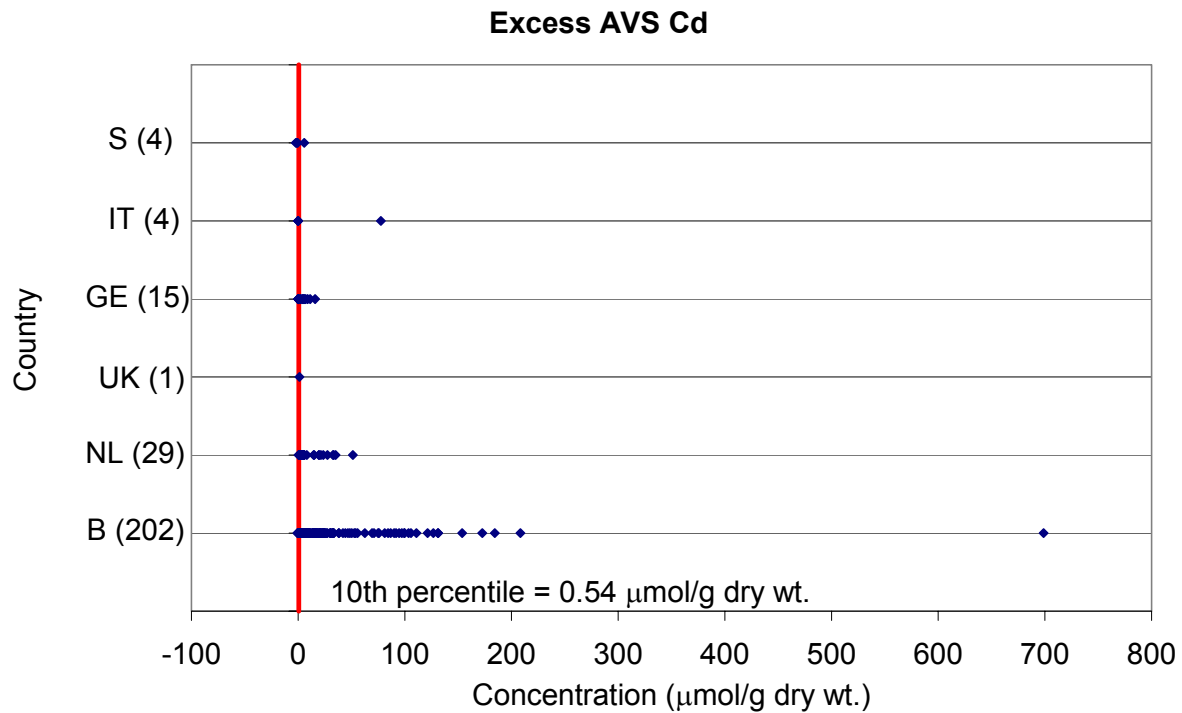


Figure 3.2.3: Overview  $\Delta AVS_{Cd}$  (AVS total  $-SEM_{Cu} - SEM_{Pb}$ ) data for all individual sampling points from Belgium (Flanders), the Netherlands, Germany, Italy and Sweden

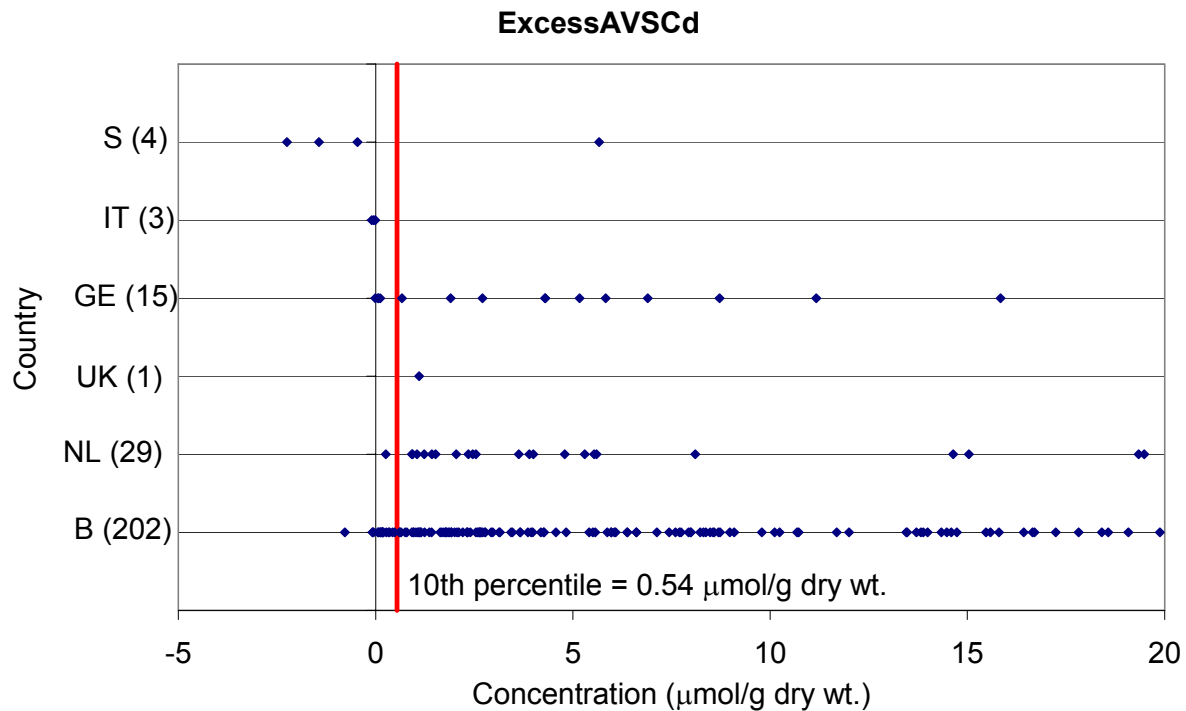


Figure 3.2.4: Detailed overview of the left tail of the  $\Delta AVS_{Cd}$  (AVS total  $-SEM_{Cu} - SEM_{Pb}$ ) distribution for Belgium (Flanders), the Netherlands, Germany, Italy and Sweden.

For the Netherlands, the 10<sup>th</sup> percentile is 1 µmol/g<sub>dw</sub> (n=29). Only one point is below the default value (excess AVS Cd = 0.3 µmol/g<sub>dw</sub>). However, according to the site specific SEM

information no excess cadmium is predicted to occur in any of the Dutch sampling stations (excess Cd < 0).

Data for Germany are available for Schmallerberg and two other river systems (local sites of Zn RAR, names not given because of confidentiality reasons). Only one measurement of available AVS for Schmallerberg is below the 10<sup>th</sup> percentile of EU (0.39 µmol/g dry wt) whereas 3 of the 5 values of  $\Delta AVS_{Cd}$  in the 2 other rivers are below. Looking at the actual site specific Cd concentrations only one site has bioavailable Cd. All other Cd is bound. The 10<sup>th</sup> percentile of the  $\Delta AVS_{Cd}$  is 0.061 µmol/g<sub>dw</sub>. The uncertainty of the regional 10<sup>th</sup> percentile of  $\Delta AVS_{Cd}$  is obviously large because it is based on only 3 rivers.

With regard to the Swedish data, three sites belonging to Lake Mälaren have no excess AVS to bind with cadmium. Important to note is that two of these sites represent contaminated sites where the elevated SEM is the cause of the low excess AVS cadmium (SEM copper values ranging from 2.2-3.3 µmol/g dry wt). The reference location has a normal copper concentrations 0.46 µmol/g dry wt but in combination with a low AVS concentration of 0.11 µmol/g<sub>dw</sub> no AVS is left to bind with cadmium. From a risk assessment perspective only the two contaminated Swedish sites will be identified as having a risk since excess SEM Cd concentrations (0.03 µmol/g<sub>dw</sub>) are above the PNEC Cd of 0.013 µmol/g<sub>dw</sub>. The derivation of a 10<sup>th</sup> percentile of  $\Delta AVS_{Cd}$  is not possible from only 4 data points that, moreover, contain 2 datapoints.

We propose to use the EU 10<sup>th</sup> percentile (**10<sup>th</sup> perc.  $\Delta AVS_{Cd}=0.49$  µmol/g<sub>dw</sub>**) as the basis to correct for Cd availability, followed by a sensitivity analysis, i.e. assessing the effects of using a regional specific 10<sup>th</sup> percentile (preferred) or using also using the lowest **10<sup>th</sup> perc.  $\Delta AVS_{Cd}=0.061$  µmol/g<sub>dw</sub>** from Germany. This RAR may have to be re-opened if new measuring data that will become available for the other metals are showing that the German data are significantly affecting the conclusion of the risk assessment.

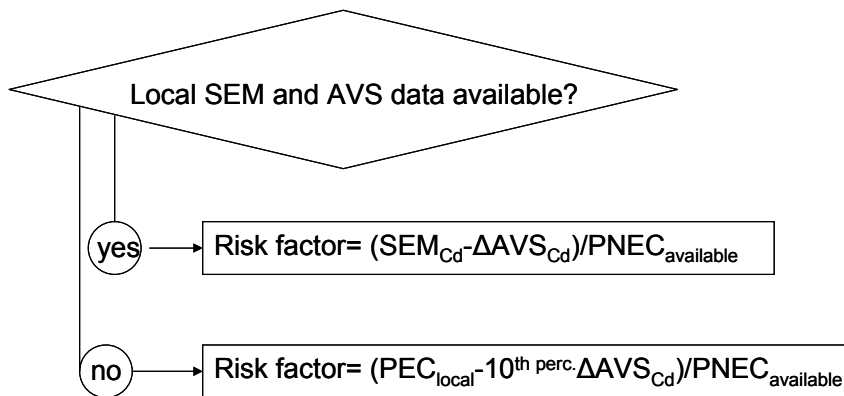
The consequence of these choices is that risk is predicted if the total Cd in sediment exceeds the sum of the 10<sup>th</sup> percentile of  $\Delta AVS_{Cd}$  (0.49 µmol/g<sub>dw</sub>= 55.4 mg Cd/kg<sub>dw</sub>) and the  $PNEC_{sediment,available}=1.5$  mg Cd/kg<sub>dw</sub>, i.e. at  $PEC_{sediment} >56.9$  mg Cd/kg<sub>dw</sub>. It should be noted that no chronic adverse effects have been observed in Cd spiked anoxic sediments in the field at total Cd concentrations below this value (Table 3.2.1 and Fig. 3.2.1)). When using the lowest 10<sup>th</sup> percentile of  $\Delta AVS_{Cd} = 0.061$  µmol/g<sub>dw</sub>, this corresponds to a  $PEC_{sediment}$  of 8.4 mg/kg. In summary, this leads to the following situation for the risk characterisation: for regions with a  $PEC_{sediment} <8.4$  mg/kg, conclusion (ii) applies. For regions with a  $PEC_{sediment} \geq 56.9$  mg/kg, conclusion (iii) applies. For regions with a  $PEC_{sediment}$  between 8.4 mg/kg – 56.9 mg/kg, conclusion (iii) applies with the note that this only holds only if the lowest 10<sup>th</sup> percentile of available AVS is used. Conclusion (ii) may be applied for these cases if regional specific AVS data are available.

There is concern that dredging of sediments could result in a potential increase in dissolved concentrations of metals in the surface water, primarily related to environmental conditions promoting the shift of trace metals from the particulate state to the dissolved state, e.g. by oxidation of reduced phases. Dredging activities are typically intermittent processes in which increased turbidity levels already quickly return to the natural background situation after 30-45 minutes (Van Parys et al., 2001) it is not expected that remobilisation of metals will occur to a large extent. Van Den Berg et al (2001b) collected data on remobilisation during a large scale experimental dredging project conducted under field conditions. The results showed that dredging activities do not notably influence dissolved concentrations of trace metals in the water

column. For an overview of similar studies (e.g Gambrell et al, 1976 etc.) supporting these observations the reader is referred to the sediment review paper by Burton et al (1991).

### 3.2.3.5 The implementation of the AVS theory for the risk assessment of Cd in sediments at the local scale

Local risk characterisation should preferentially be based on measured values of SEM and AVS and it is recommended that surface sediments should be sampled. In the absence of these data, risk factors will be based on a realistic worst case 'available' AVS concentration, similarly selected as in the regional risk characterisation (see above). This scheme is



The 10<sup>th</sup> perc.ΔAVS is the 10<sup>th</sup> percentile of the concentrations of available AVS ( $\Delta\text{AVS}=0.49 \mu\text{mol/g}_{\text{dw}}$ ) in EU freshwater systems as derived above, followed by a sensitivity analysis, i.e. assessing the effects of also using the lowest 10<sup>th</sup> perc.  $\Delta\text{AVS}_{\text{Cd}}=0.061 \mu\text{mol/g}_{\text{dw}}$  from Germany. This scheme is identical to that in the regional approach described above. We note that this is a conservative approach (Fig. 3.2.4)

### 3.3 RISK CHARACTERISATION

#### 3.3.1 Introduction

The risk characterisation is based on a comparison of the PEC with PNEC values. Table 3.3.1 summarises the PNEC values that were calculated in the effects assessment (section 3.2 of the overall RAR on Cd/CdO).

**Table 3.3.1: the PNEC values for water and sediment**

	value	units	remark
PNEC <sub>water</sub>	0.19	µg Cd L <sup>-1</sup>	dissolved fraction
PNEC <sub>water</sub>	0.09 * (H/50) <sup>0.7409</sup>	µg Cd L <sup>-1</sup>	for refined risk characterisation if hardness is known (section 3.2.1.6.4); dissolved fraction; not to be used below H=40
PNEC <sub>sediment,available</sub>	0.013	µmol g <sup>-1</sup> <sub>dw</sub>	AVS based normalisation is used for regional as well as site-specific risk characterisation
	1.5	mg kg <sup>-1</sup> <sub>dw</sub>	

### 3.3.2

## The aquatic compartment (including sediment and STP)

### 3.2.3.1 Local scenarios

#### 3.2.3.1.1 Scenarios of the 'overall' RAR (reference year: 1996, in general)

The risk factors (PEC/PNEC ratio) for **local water** (dissolved fraction) and **sediment** concentrations are given in Table 3.3.2. The PNEC was not corrected for water hardness because of lack of site-specific water hardness information. The corrections for bioavailability of Cd in sediments were made using the default  $\Delta AVS_{Cd}$  value of  $0.49 \mu\text{mol/g}_{dw}$  because of lack of site-specific information.

**Table 3.3.2: Local risk characterisation for water and sediment. The factor risk = PEC/PNEC. The  $PNEC_{water}$  is  $0.19 \mu\text{g Cd L}^{-1}$  and the  $PNEC_{sediment,available}$  is  $0.013 \mu\text{mol Cd g}^{-1}_{dw}$ . (Table 3.3.1). The factor risk for sediments is calculated for the concentration of added+regional Cd (total Cd, i.e.  $PEC_{local,sediment}$ , Table 3.1.7 of the overall RAR on Cd/CdO, converted to molar units and corrected for AVS reducing the Cd bioavailability; i.e. risk =  $(PEC/112-0.49)/0.013$ ; risk factors  $<0$  were set to 0). Risk identified in sediment by using a lower estimate for bioavailability correction is indicated by<sup>s</sup>.**

use- Category	N°	$PEC_{local,water}$ $\mu\text{g L}^{-1}$	factor risk water	$PEC_{local,sediment}$	factor risk sediment total	year
Cd-production	1	1.37	<b>7.2</b>	166.4	<b>76.6</b>	1996
	2	0.59	<b>3.1</b>	64.1	<b>6.3</b>	1996
	3*	0.15*	0.8*	7.1	0	1996
	4*	0.52*	<b>2.7*</b>	55.6	<b>0-33.5<sup>s</sup></b>	1996
	5	5.5	<b>29</b>	707.8	<b>448.4</b>	1996
	6	0.11	0.6	2.7	0	1996
	7 <sup>fc</sup>	0.32*	<b>1.7*</b>	29.1	<b>0-15.2<sup>s</sup></b>	1996
	8	0.12	0.7	4.1	0	1996
	9*	0.13*	0.7*	4.5	0	1999
	10	0.11	0.6	2.7	0	1996
	11	0.11	0.6	2.7	0	1996
	13*	0.69*	<b>3.6*</b>	77.6	<b>15.6</b>	1996
	CdO-producers	11	0.11	0.6	2.7	0
12		0.11	0.6	2.7	0	1993
Cd-stabilisers	F	0.11	0.6	2.8	0	1996
	G	0.29	<b>1.5</b>	25.6	<b>0-12.8<sup>s</sup></b>	1996
	H	0.14	0.7	6.2	0	1996
	I	0.13	0.7	4.4	0	1996
	J	0.11	0.6	2.7	0	1996
	K	0.69	<b>3.6</b>	78.0	<b>15.8</b>	1996
	L	0.11	0.6	2.7	0	1996
	M	0.11	0.6	2.7	0	1996
windows manufacturer		0.11	0.6	2.7	0	1996
Cd-pigments	A	0.26	<b>1.4</b>	21.5	<b>0-10.0<sup>s</sup></b>	1996
	B	0.11	0.6	2.8	0	1996
	C	0.15	0.8	7.9	0	1996
	D	0.14	0.8	6.5	0	1996
	E	0.11	0.6	2.8	0	1996
Cd-plating	EU	2.9	<b>15</b>	359.6	<b>209.3</b>	1996

use- Category	N°	PEC <sub>local</sub> <sub>water</sub> µg L <sup>-1</sup>	factor risk water	PEC <sub>local</sub> <sub>sediment</sub>	factor risk sediment total	year
Cd-alloys	EU	1.81	9.5	223	115.5	1996

\*Emission to the sea; n.a.: not available; †: recently delivered data were not yet taken into account, this will be done during the development of the Risk Reduction Strategy. ‡sensitivity analysis: risk identified if the lowest regional specific value would have been used ( $\Delta AVS_{Cd}=0.061 \mu\text{mol/g}_{dw}$ )

The table predicts elevated risks for the aquatic ecosystem at 11 locations/scenarios and risk to benthic organisms at 7 sites/scenarios. The risk for the Cd alloy processing sites is based on a generic scenario (see 3.1.2.1 of the overall RAR on Cd/CdO).

The risks for **benthic organisms** are elevated at 7 sites/scenarios. The risk characterisation could be refined by including indicators of Cd bioavailability. This can be achieved by measuring the excess of SEM over AVS. This refinement should use a worst case approach to account for seasonal and spatial variation in AVS, i.e. sample the surface sediment in spring season.

*Sensitivity analysis* about the choice of available AVS to correct for bioavailability: the risk characterisation derived here uses a default 10<sup>th</sup> percentile of the EU based value for available AVS ( $\Delta AVS_{Cd}=0.49 \mu\text{mol/g}_{dw}$ ). If the lowest regional specific value would have been used ( $\Delta AVS=0.061 \mu\text{mol/g}_{dw}$ ), then risk is elevated at 4 more sites (indicated by † sign after risk factor), but all these 4 sites also have a risk for the aquatic system, **i.e. the uncertainty about the value of the regional 10 percentile of  $\Delta AVS_{Cd}$  does not affect the number of local sites at which local risk is identified.** It can be shown that is also true for almost all other local sites described below.

### 3.2.3.1.2 Scenarios of the TRAR (reference year: 1999/2000, in general)

The risk factors (PEC/PNEC ratio) for **local water** and **sediment** concentrations are given in Table 3.3.3 for the Ni-Cd producers and recyclers and in Tables 3.3.6, 3.3.7, 3.3.8 and 3.3.9 for incinerators and landfills. By lack of relevant data, corrections for water hardness could not be done for the risk characterisation.

### Ni-Cd producing/recycling plants

**Table 3.3.3: Local risk characterisation Ni-Cd producing/recycling plants for water, sediment and STP. The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. The PNEC for micro-organisms is 20 µg/L (Table 3.3.1). Risk identified in sediment by using a lower estimate for bioavailability correction is indicated by ‡.**

use- Category	N°	PEC <sub>local</sub> water site specific µg/L	factor risk water site specific	PEC <sub>local</sub> water DF=1,000 µg/L	factor risk water DF=1,000	PEC <sub>local</sub> sediment DF=1,000 or site specific mg/kg dw	factor risk sediment DF=1,000 or site specific Total	C <sub>effluent</sub> (mg/L)	Factor risk STP	year
NiCd-batteries	1	0.12	0.63	N/A	N/A	3.2	0	0.019 <sup>a</sup>	0.95	1999
	2*	0.15	0.79	0.15	0.79	8.0	0	0.12	n.r	2000

use-	N°	PEClocal water site specific	factor risk water site specific	PEClocal water DF=1,000	factor risk water DF=1,000	PEClocals ediment DF=1,000 or site specific	factor risk sediment DF=1,000 or site specific Total	C <sub>effluent</sub>	Factor risk STP	year
Category		µg/L		µg/L		mg/kg dw		(mg/L)		
	3	0.12	0.63	0.15	0.79	8.0	0	0.12	n.r.	2000
	4	0.18	0.94	N/A	N/A	10.5	0-2.5 <sup>s</sup>	0.13	n.r.	2000
	5	0.11	0.58	0.114	0.58	2.7	0	0.00007 <sup>a</sup>	0.005	2000
	6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	n.r.	1999
	7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	n.r.	1999
Cdrecyclers	1 <sup>b</sup>	0.19	1.0	0.27	1.4	22.6	0-10.8 <sup>s</sup>	0.45	n.r.	2000
	1 <sup>c</sup>	0.13	0.68	0.17	0.89	19.8	0-8.9 <sup>s</sup>	0.17	n.r.	2000
	2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1999

N/A: not applicable, <sup>a</sup> influent concentration STP = effluent concentration plant\*DF STP)

<sup>b</sup> based on P90 of daily measurements, <sup>c</sup> based on average effluent concentration and average effluent flow rate

n.r.: not relevant. \* emission to the sea; <sup>s</sup>sensitivity analysis: risk identified if the lowest regional specific value would have been used ( $\Delta AVS_{Cd}=0.061 \mu\text{mol/g}_{dw}$ )

Since site specific information on SEM/AVS is lacking for Ni-Cd batteries and Cd recycling sites, risk factors are based on a default 10th percentile of ‘available’ AVS concentration or a lower value (indicated by <sup>s</sup>). No risk is predicted for all but two sites.

### MSW incinerators

**Table 3.3.4: Local risk characterisation incinerators for sediments (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. Total cadmium.**

	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total	PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total
	mg/kg dw	-	mg/kg dw	-
Scenario 1/2	5.19	0	2.91	0

Incorporating the default sediment bioavailability correction (reasonable worst case ‘available’ AVS concentration i.e.  $0.49 \mu\text{mol/g}_{dw} = 10P \Delta AVS$ ) results in no risk for sediment organisms for all hypothetical local incineration scenarios (risk factor = 0).

**Table 3.3.5: Local risk characterisation incinerators for sediments (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. Total cadmium without Ni-Cd contribution**

	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total		PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total	
	mg/kg dw	-	-	mg/kg dw	-	
	Assumption Ni-Cd batteries contributed 10 % to the overall Cd load					
Scenario 1/2	4.87	0		2.69	0	
	Assumption Ni-Cd batteries contributed 50 % to the overall Cd load					



	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total		PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total	
	mg/kg dw	-	-	mg/kg dw	-	
Scenario 1/2	3.93	0		2.79	0	

Removing all Ni-Cd batteries from the MSW stream results in the same conclusions: no risk is observed.

## **Future scenarios and sensitivity analysis MSW incinerators**

### **Future scenario**

For none of the future scenarios a risk is predicted for sediment organisms (bioavailability correction incorporated; reasonable worst case 'available' AVS concentration i.e.  $0.49 \mu\text{mol/g}_{\text{dw}}$  =  $10P \Delta\text{AVS}$ ).

**Table 3.3.6: Local risk characterisation incinerators for sediments for a generic MSW incineration plant in the EU. Future scenarios: collection rate: 10 and 75% (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. Total cadmium.**

Scenario	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total	PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total
	mg/kg dw	-	mg/kg dw	-
MSW Incineration plant (10%; total cadmium)	8.6	0-1.2 <sup>§</sup>	3.03	0
MSW Incineration plant (75%; total cadmium)	6.8	0	3.0	0

; <sup>§</sup>sensitivity analysis: risk identified if the lowest regional specific value would have been used ( $\Delta AVS_{Cd}=0.061 \mu\text{mol/g dw}$ )

## Sensitivity analysis

**Table 3.3.7: Local risk characterisation incinerators for sediments for a generic MSW incineration plant in the EU. Sensitivity analysis: effluent = 0.009 mg/L. (at dilution factor 100 and 1,000). The factor risk = PEC/PNEC. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. Total cadmium.**

Scenario	PEC local sediment DF = 100	Factor risk sediment DF = 100 Total	PEC local sediment DF = 1,000	Factor risk sediment DF = 1,000 Total
	mg/kg dw	-	mg/kg dw	-
MSW Incineration plant (10%; total cadmium)	6.6	0	3.05	0

No risk is predicted for sediment organisms..

## MSW landfills

**Table 3.3.8: Local risk characterisation landfills (leachate concentration 5 µg/L) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. The PNEC for micro-organisms is 20 µg/L (Table 3.3.1). Total cadmium**

use-category	N°	PEC <sub>local water</sub>	factor risk water	PEC <sub>local sediment</sub>	factor risk sediment Total	C <sub>effluent</sub>	Factor risk STP
		µg/L		mg/kg dw		mg/L	
MSW landfill (total cadmium)	1	0.12	0.63	3.8	0	0.005	n.r.
MSW landfill (total cadmium)	2	0.12	0.63	3.1	0	0.00024 <sup>a</sup>	0.012

n.r. = not relevant

a = 5 µg/L / 21 (21 being the dilution factor in STP cfr Table 3.1.89)

No risks to the aquatic environment (water and sediment) are observed for landfills emitting a leachate with total cadmium content of 5 µg/L.

In Table 3.3.9 the RCR values for the scenario where all Ni-Cd batteries would be removed from the MSW stream is given. The influence on the RCR values is negligible.

**Table 3.3.9: Local risk characterisation landfills (leachate concentration 5 µg/L) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw. The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. The PNEC for micro-organisms is 20 µg/L (Table 3.3.1). All cadmium without Ni-Cd batteries**

use-category	N°	PEC <sub>local</sub> water	factor risk water	PEC <sub>local</sub> sediment	factor risk sediment Total
		µg /L		mg/kg dw	
MSW Landfill (Ni-Cd batteries contributed for 10 %)	1	0.12	0.63	3.7	0
MSW Landfill (Ni-Cd batteries contributed for 50 %)		0.12	0.63	3.3	0
MSW Landfill (Ni-Cd batteries contributed for 10 %)	2	0.12	0.63	3.1	0
MSW Landfill (Ni-Cd batteries contributed for 50 %)		0.12	0.63	2.9	0

*n.r.* = not relevant

*a* = 5 µg/L / 21 (21 being the dilution factor in STP cfr Table 3.1.89)

## Sensitivity analysis

**Table 3.3.10: Local risk characterisation landfills (leachate concentration 50 µg/L) for water, sediment and STP. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw. The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. The PNEC for micro-organisms is 20 µg/L (Table 3.3.1).**

use-category	N°	PEC <sub>local</sub> water	factor risk water	PEC <sub>local</sub> sediment	factor risk sediment Total	C <sub>effluent</sub>	Factor risk STP
		µg/L		mg/kg dry wt		mg/L	
MSW landfill (total cadmium)	1	0.21	1.1	14.9	0-5.5 <sup>§</sup>	0.050	n.r.
MSW landfill (total cadmium)	2	0.15	0.79	6.8	0	0.0024 <sup>a</sup>	0.12

*n.r.* = not relevant; *a* = 50 µg/L / 21 (21 being the dilution factor in STP cfr Table 3.1.89); <sup>§</sup>sensitivity analysis: risk identified if the lowest regional specific value would have been used ( $\Delta$ AVS<sub>Cd</sub>=0.061 µmol/g<sub>dw</sub>)

No risks to the aquatic environment is observed for landfills emitting a leachate with a total cadmium content of 50 µg/L to a STP. If this leachate concentration is discharged immediately to the surface water a risk is predicted for the scenario ‘all cadmium in MSW’. No risk is predicted for all scenarios for the sediment compartment after accounting for bioavailability, except when a low value of a regional available AVS is selected

**Table 3.3.11: Local risk characterisation landfills (leachate concentration 50 µg/L) for water and sediment. Scenario 1 = direct discharge to surface water. Scenario 2 = indirect discharge to surface water (STP). The factor risk = PEC/PNEC. The PNEC<sub>water</sub> is 0.19 µg Cd/L. The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0. The PNEC for micro-organisms is 20 µg/L (Table 3.3.1). Total cadmium without Ni-Cd batteries**

use-category	N°	PEC <sub>local water</sub>	factor risk water	PEC <sub>local sediment</sub>	factor risk sediment Total
		µg /L		mg/kg dw	
MSW Landfill (Ni-Cd batteries contributed for 10 %)	1	0.20	1.1	13.7-	0-4.7 <sup>s</sup>
MSW Landfill (Ni-Cd batteries contributed for 50 %)		0.16	0.84	8.8	0-1.4 <sup>s</sup>
MSW Landfill (Ni-Cd batteries contributed for 10 %)	2	0.14	0.7	6.3	0
MSW Landfill (Ni-Cd batteries contributed for 50 %)		0.13	0.68	4.7	0

*n.r.* = not relevant;

*a* = 50 µg/L / 21 (21 being the dilution factor in STP cfr Table 3.1.89); <sup>s</sup>sensitivity analysis: risk identified if the lowest regional specific value would have been used ( $\Delta AVS_{Cd} = 0.061 \mu\text{mol/g}_{dw}$ )

### 3.2.3.1.3 Scenarios of the ‘overall’ RAR (reference year: 2002, in general)

The risk factors (PEC/PNEC ratio) for WWTP/STP, local water (dissolved fraction) and sediment concentrations are given in Table 3.3.12. The PNEC<sub>water</sub> is not corrected for water hardness because of lack of site-specific water hardness information.

**Table 3.3.12: Local risk characterisation of Cd/CdO production/processing sites for WWTP/STP, water and sediment (modelled data). The factor risk = PEC/PNEC. The PNEC<sub>micro-organisms</sub> is 20 µg/l, The PNEC<sub>water</sub> is 0.19 µg Cd L<sup>-1</sup> and The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0.**

plant N°	PEC <sub>wwtp/stp</sub> (dissolved fraction)	factor risk wwtp/stp	PEC <sub>local water</sub> (dissolved Cd)	factor risk water	PEC <sub>local sediment</sub>	factor risk sediment (total)	year
	µg L <sup>-1</sup>		µg L <sup>-1</sup>		mg kg <sup>-1</sup> <sub>dw</sub>		
Cd metal production							
1	3.6 <sup>(d)</sup>	0.18	0.64	3.36	71.5 <sup>(f)</sup>	- <sup>(f)</sup>	2002
6	0.7	0.04	0.11	0.58	2.7	0	2002
7*	50	2.48	0.28	1.46	24.5	0-12.1 <sup>s</sup>	2002

plant N°	PEC <sub>wwtp/stp</sub> (dissolved fraction)	factor risk wwtp/stp	PEC <sub>local<sub>water</sub></sub> (dissolved Cd)	factor risk water	PEC <sub>local<sub>sediment</sub></sub>	factor risk sediment (total)	year
	µg L <sup>-1</sup>		µg L <sup>-1</sup>		mg kg <sup>-1</sup> <sub>dw</sub>		
Cd oxide production							
12 <sup>(a)</sup>	0	0	0.11	0.58	2.7	0	2002
Cd pigments production							
A	19	0.94	0.38	<b>1.98</b>	37.4	<b>0-20.9<sup>s</sup></b>	2003
B	19	0.95	0.12	0.61	3.5	0	2003
C	121	<b>6.03</b>	0.25	<b>1.32</b>	21.0	<b>0-9.7<sup>s</sup></b>	2003
C(90P)	80	<b>4.0</b>	0.25	<b>1.34</b>	21.3	<b>0-9.9<sup>s</sup></b>	2004
Cd stabiliser production							
X WWTP	5	0.25					
X STP©	0.4	0.02	0.11	0.58	2.7	0	2002
Y	5	0.25	0.12	0.62	3.6	0	2002

\*Emission to the sea; n.a.: not available; (a) No emission to water; thermal/dry process; (b) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant. c) Cd concentration in effluent from municipal STP; calculated from Cd concentration in effluent from on site WWTP; taking into account removal at STP: 60%; extra dilution: 2000 m<sup>3</sup>/d/370 m<sup>3</sup>/d = 5.4. (d) the biological based wastewater purification system contains fully adapted, specialised and dedicated micro-organisms. These bacteria are not at all representative for 'standard' micro-organisms communities used in municipal STPs. (e) Emissions from the site are further reduced in 2003/2004 due to efforts to conform to ISO 14000, for which the site has been certified in February 2005. (f) for this site measured values on SEM and AVS are available, these values are used instead of modelled PEC<sub>sediment</sub> (see Table 3.3.13). <sup>s</sup>sensitivity analysis: risk identified if the lowest regional specific value would have been used ( $\Delta AVS_{Cd}=0.061 \mu\text{mol/g}_{dw}$ ).

## Benthic organisms

For Cd metal production site 1 measured values on SEM and AVS are available, hence the correction is based on the site specific measured data (risk factor =  $(SEM_{Cd} - \Delta AVS_{Cd})/PNEC_{available}$ ). An overview of the available data is provided in Table 3.3.13. From this table it can be concluded that since for both sampling points  $\Delta AVS_{Cd}$  exceeds  $SEM_{Cd}$ , all Cd will be bound to AVS and will not be bioavailable. The difference in AVS content upstream and downstream can be explained by the recent dredging activities (Heijerick & Vangheluwe, 2003).

**Table 3.3.13 Overview of measured SEM/AVS values, PEC<sub>available</sub> and risk factor for Cd metal production site 1. Negative risk factors are set to 0.**

	SEM <sub>Cd</sub> (µmol/g <sub>dw</sub> )	$\Delta AVS_{Cd}=AVS_{total}-SEM_{Cu}-SEM_{Pb}$ (µmol/g <sub>dw</sub> )	PEC <sub>available</sub> =SEM <sub>Cd</sub> - ΔAVS <sub>Cd</sub> (µmol/g <sub>dw</sub> )	Risk factor =PEC <sub>available</sub> /PNEC <sub>available</sub>
Upstream	0.04	23.46 = 23.7-0.02-0.22	-23.42	0
Downstream	0.01	2.54=2.6-0.03-0.03	-2.53	0

For all other production and processing sites, no site specific information on AVS/SEM is available, hence the sediment bioavailability corrections made are based on the default EU  $\Delta AVS$  of 0.49 µmol/g<sub>dw</sub>.

From Tables 3.3.12 and 3.3.13 it can be concluded that for none of the Cd metal/CdO producing or processing sites, a risk for sediment organisms is predicted (risk factors = 0) except when a low value of a regional available AVS is selected.

### 3.2.3.1.4 Scenarios of the TRAR (reference year: 2002, in general)

The risk factors (PEC/PNEC ratio) for WWTP/STP, local water (dissolved fraction) and sediment concentrations are given in Table 3.3.14. The PNEC<sub>water</sub> is not corrected for water hardness because of lack of site-specific water hardness information.

**Table 3.3.14: Local risk characterisation of Cd/CdO production/processing sites for WWTP/STP, water and sediment (modelled data). The factor risk = PEC/PNEC. The PNEC<sub>micro-organisms</sub> is 20 µg/l, The PNEC<sub>water</sub> is 0.19 µg Cd L<sup>-1</sup> and The PNEC<sub>sediment, available</sub> is 0.013 µmol Cd/g dw The factor risk is calculated for the added+regional Cd (total Cd, i.e. PEC<sub>sediment</sub>), converted to molar units and corrected for AVS reducing the Cd bioavailability, i.e. risk= (PEC/112-0.49)/0.013; risk factors <0 were set to 0.**

plant N°	PEC <sub>wwtp/stp</sub> (dissolved fraction)	factor risk wwtp/stp	PEC <sub>localwater</sub> (dissolved Cd)	factor risk water	PEC <sub>localsediment</sub>	factor risk sediment (total)	year
	µg L <sup>-1</sup>		µg L <sup>-1</sup>		mg kg <sup>-1</sup> <sub>dw</sub>		
Ni-Cd battery production							
2*	107	<b>5.34</b>	0.15	0.77	7.4	0	2002
3	63	<b>3.17</b>	0.13	0.69	5.5	0	2002
4	103	<b>5.16</b>	0.14	0.76	7.2	0	2002
6	No update data						
7	No update data						
Ni-Cd battery recycling							
1	370	<b>18.5</b>	0.24	<b>1.24</b>	19.0	<b>0-8.3<sup>§</sup></b>	2002
1 <sup>(e)</sup>	240	<b>12.0</b>	0.19	<b>1.01</b>	13.2	<b>0-4.3<sup>§</sup></b>	2004
2 <sup>(b)</sup>	0	0	0.11	0.58	2.7	0	2002

\*Emission to the sea; n.a.: not available; (a) No emission to water; thermal/dry process; (b) No site emission to water. Cleaning water as well as processing water are collected internal (about 100 m<sup>3</sup>/year) and send to an external waste water treatment plant. c) Cd concentration in effluent from municipal STP; calculated from Cd concentration in effluent from on site WWTP; taking into account removal at STP: 60%; extra dilution: 2000 m<sup>3</sup>/d/370 m<sup>3</sup>/d = 5.4. (d) the biological based wastewater purification system contains fully adapted, specialised and dedicated micro-organisms. These bacteria are not at all representative for 'standard' micro-organisms communities used in municipal STPs. (e) Emissions from the site are further reduced in 2003/2004 due to efforts to conform to ISO 14000, for which the site has been certified in February 2005. <sup>§</sup>sensitivity analysis: risk identified if the lowest regional specific value would have been used ( $\Delta$ AVS<sub>Cd</sub>=0.061 µmol/g<sub>dw</sub>)

For all Ni-Cd battery producing and recycling sites, no site specific information on AVS/SEM is available, hence the sediment bioavailability corrections made are based on default  $\Delta$ AVS<sub>Cd</sub> of 0.49 µmol/g<sub>dw</sub>.

From Table 3.3.14 it can be concluded that for none of the Ni-Cd battery producing and recycling sites a risk for sediment organisms is predicted (risk factors = 0) except when a low value of a regional available AVS is selected where some sites show risk for sediment organisms as well as for the aquatic system.

### 3.2.3.2 Regional and continental Cd concentrations

#### Calculated values:

The predicted concentrations in sediment have also been calculated for a range in K<sub>p</sub> values (Table 3.1.15). The following values were obtained for the regional and continental scale respectively: 3.88 mg/kg ww (2.70-4.01 mg/kg ww) and 1.25 mg/kg ww (1.16-1.25 mg/kg ww).

The bioavailability corrected PEC/PNEC sediment ratios of 0 for both continental and regional PECs illustrate that no risk is predicted unless the  $\Delta AVS_{Cd}$  is low: at the lowest regional 10<sup>th</sup> percentile of  $\Delta AVS_{Cd}=0.061 \mu\text{mol/g}_{dw}$ , risk can not be excluded at the regional scale using the mean or a higher value of the Kp (risk factors 2.1-2.4).

*Measured values:* it is proposed to refine the risk characterisation with measured data which may be more relevant given the uncertainties in emissions, their geographical distribution, the wide range in natural environments, contributions from historic pollution etc.

*Sediment:*

**Table 3.3.15: regional risk characterisation for sediment. The factor risk =  $((PEC-\Delta AVS_{Cd})/PNEC_{\text{sediment,available}})$ . The  $PNEC_{\text{sediment,available}}$  is  $0.013 \mu\text{mol Cd g}^{-1}_{dw}$  ( $1.5 \text{ mg Cd kg}^{-1}_{dw}$ ) and the corresponding regional  $\Delta AVS_{Cd}$  as given.**

	n	90 <sup>th</sup> percentile [mg Cd kg <sup>-1</sup> <sub>dw</sub> ]	$\Delta AVS_{Cd}$ $\mu\text{mol/g}_{dw}$	Factor risk	supporting information: inclusion of outliers		
					90 <sup>th</sup> percentile [mg Cd kg <sup>-1</sup> <sub>dw</sub> ]	$\Delta AVS_{Cd}$ $\mu\text{mol/g}_{dw}$	Factor risk
Belgium (VMM)	512	1.59	0.54	0	1.75	0.54	0
France	315	2.86	0.061-0.49	0-0	3.86	0.061-0.49	0
France - Artois-Picardie	126	2.05	0.061-0.49	0-0	37	0.061-0.49	0-20.6
France- Rhône-Méditerranée	66	0.93	0.061-0.49	0-0	0.93	0.061-0.49	0
Spain	8	2.20	0.061-0.49	0-0	8.3	0.061-0.49	0-1.0
Sweden	297	2.97	0.061-0.49	0-0	2.97	0.061-0.49	0
The Netherlands <i>Supporting information: 90<sup>th</sup> percentile of Cd in suspended matter</i>	18	3.69 8.5	1.0	0 0	11.48	1.0	0

The limited data presented in Table 3.3.15 show risk factors of 0 for the sediment compartment; hence no risk is predicted with the exception of a French region (Artois Picardie) if outliers are included in the data. That area is known for historical contamination by former non-ferrous metal smelters and the original data show that the outliers, detected by statistical analysis, are mainly located on the Deule channel (Canal de la Deule) with total Cd >1000 mg Cd/kg. Moreover, unpublished data of AVS concentrations in that river show total AVS >10  $\mu\text{mol/g}_{dw}$ , i.e. the application of a lower value of  $\Delta AVS_{Cd}$  ( $0.06 \mu\text{mol/g}_{dw}$  from German rivers) to correct for Cd bioavailability in these locally contaminated rivers is not appropriate. Because of the local nature of this contamination, we propose that these outliers do not represent diffuse contamination at the regional scale and that the outliers should be excluded. Therefore, a conclusion (ii) is proposed for Cd in sediment at the regional scale.

### 3.2.3.3 Sediment compartment

#### Conclusions to the risk assessment for the sediment compartment:

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to:

- 4 Cd metal/CdO production plants, 1 Cd stabiliser producing plant included in the overall Cd/CdO RAR (reference year 1996). Data and assessment regards these scenarios are overwritten by the results of the update document (reference year 2002) see under conclusion ii)
- Cd plating sector and Cd alloys sector included in the overall Cd/CdO RAR (reference year 1996). For these scenarios no new exposure data were submitted.
- Risk is additionally identified for the benthic organisms at 4 sites<sup>2</sup> and 4 disposal scenarios if the lowest regional 10<sup>th</sup> percentile (German data from 3 river systems) from the AVS database is used for the bioavailability correction instead of the 10<sup>th</sup> percentile of the entire EU AVS data which are dominated by data from NL and BE. The 4 sites and 4 scenarios are:
  - o 1 Cd metal production site, 2 Cd pigments production sites (update RAR Cd/CdO, year 2002);
  - o 1 Cd recycler (update RAR Cd/CdO year 2002);
  - o 1 MSW incineration scenario (future scenario), 3 MSW landfill scenarios.

**Conclusion (ii)** There is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already.

This conclusion applies to:

- 6 Cd metal production plants, 2 CdO production plants, 6 Cd stabiliser producing plants and 5 Cd pigments producing plants included in the original Cd/CdO RAR (reference year 1996). Data and assessment regards these scenarios are overwritten by the results of the update document of the RA on Cd/CdO (reference year 2002), see here below
- 3 Cd metal/CdO production plants, 1 Cd pigments producing plants, 2 Cd stabiliser producing plants that are included in the update document of the RA on Cd metal/CdO (reference year 2002).
- 4 Ni-Cd battery production plants that are included in the TRAR (reference year 1999/2000).
- Most present and future scenarios, except 4, for local incineration plants and MSW landfill sites included in the TRAR (reference year 1999/2000).
- 3 Ni-Cd battery production and 1 recycling plants that are included in the update TRAR (reference year 2002).

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<sup>2</sup> based on results from the update document of the RA on Cd/CdO, reference year 2002 only. As mentioned above, the results from the 1996 (Cd/CdO production and processing sites); 1999/2000 (Ni-Cd battery producers/recyclers) assessments are overwritten by the results of the update document of the RA on Cd/CdO (reference year 2002)



- Measured regional and continental Cd concentrations in sediments based on 90<sup>th</sup> percentiles of regional Cd data from Belgium, France, Spain, Sweden and The Netherlands.

The Cd bioavailability has been taken into account for deriving this conclusion (ii). Without such correction, regional and local risk is predicted in some of these regions/locations. The bioavailability correction is based on the concentration of available acid volatile sulphides (AVS) in the sediment, which reduce the toxicity in sediment (i.e. reduced risk with increasing AVS concentration). The AVS concentration is the 10<sup>th</sup> percentile of regional values (for Belgium and The Netherlands) and, for other regions and all local sites, the lowest regional 10<sup>th</sup> percentile of the EU regions (German data from 3 river systems). That 10<sup>th</sup> percentile may be revised (and conclusions as well) if other AVS data become available which is recommended given the relatively limited EU coverage of regional AVS data (only 6 countries).

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# GLOSSARY

<b>Standard term / Abbreviation</b>	<b>Explanation/Remarks and Alternative Abbreviation(s)</b>
<i>Ann.</i>	Annex
AF	assessment factor
BCF	bioconcentration factor
bw	body weight / <i>Bw, b.w.</i>
°C	degrees Celsius (centigrade)
CAS	Chemical Abstract System
CEC	Commission of the European Communities
CEN	European Committee for Normalisation
CEPE	European Council of the Paint, Printing Ink and Artists' Colours Industry
d	day(s)
d.wt	dry weight / <sub>dw</sub>
DG	Directorate General
DT <sub>50</sub>	period required for 50 percent dissipation (define method of estimation)
DT <sub>50lab</sub>	period required for 50 percent dissipation under laboratory conditions (define method of estimation)
DT <sub>90</sub>	period required for 90 percent dissipation (define method of estimation)
DT <sub>90field</sub>	period required for 90 percent dissipation under field conditions (define method of estimation)
EC	European Communities
EC	European Commission
EC <sub>50</sub>	median effective concentration
EEC	European Economic Community
EINECS	European Inventory of Existing Commercial Chemical Substances
EU	European Union
EUSES	European Union System for the Evaluation of Substances
f <sub>oc</sub>	Fraction of organic carbon
G	gram(s)

PNEC(s)	Predicted No Effect Concentration(s)
PNEC <sub>water</sub>	Predicted No Effect Concentration in Water
(Q)SAR	Quantitative Structure Activity Relationship
STP	Sewage Treatment Plant
TGD	Technical Guidance Document <sup>3</sup>
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products or Biological material
v/v	volume per volume ratio
w/w	weight per weight ratio
w	gram weight
GLP	Good Laboratory Practice
h	hour(s)
ha	Hectares / <i>h</i>
HPLC	High Pressure Liquid Chromatography
IARC	International Agency for Research on Cancer
C <sub>50</sub>	median immobilisation concentration or median inhibitory concentration 1 / <i>explained by a footnote if necessary</i>
ISO	International Standards Organisation
IUPAC	International Union for Pure Applied Chemistry
kg	kilogram(s)
kPa	kilo Pascals
K <sub>oc</sub>	organic carbon adsorption coefficient
K <sub>ow</sub>	octanol-water partition coefficient
K <sub>p</sub>	Solids water partition coefficient
l	litre(s)
log	logarithm to the basis 10
L(E)C <sub>50</sub>	Lethal Concentration, Median
LEV	Local Exhaust Ventilation
m	Meter
µg	microgram(s)

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<sup>3</sup> Commission of the European Communities, 1996. Technical Guidance Documents in Support of the Commission Directive 93/67/EEC on risk assessment for new substances and the Commission Regulation (EC) No 1488/94 on risk assessment for existing substances. Commission of the European Communities, Brussels, Belgium. ISBN 92-827-801[1234]

mg	milligram(s)
MAC	Maximum Accessibility Concentration
MOS	Margins Of Safety
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
NOEL	No Observed Effect Level
OEL	Occupational Exposure Limit
OECD	Organisation for Economic Co-operation and Development
OJ	Official Journal
pH	potential hydrogen <i>-logarithm</i> (to the base 10) of the hydrogen ion concentration {H <sup>+</sup> }
pKa	<i>-logarithm</i> (to the base 10) of the acid dissociation constant
pKb	<i>-logarithm</i> (to the base 10) of the base dissociation constant
Pa	Pascal unit(s)
PEC	Predicted Environmental Concentration
STP	Sewage Treatment Plant
WWTP	Waste Water Treatment Plant





## Annex 1 Details of the sediment toxicity data to justify the AVS concept

Studies detailed below refer to those summarized in Table 3.2.1.

### Di Toro et al., 1990

Di Toro et al (1990) introduced and proved his SEM-AVS concept for the first time using cadmium as model toxicant. In this paper 10 d acute sediment toxicity tests with the marine amphipods *Ampelisca abdita* and *Rhepoxynius hudsoni* were performed using Cd spiked sediments. Sediments chosen were Long Island Sound sediment (US) with an average AVS concentration (i.e. 14.9  $\mu\text{mol/g}$  dry wt, average from the initial and final measured AVS values.), Ninigret Pond sediment as representative of a sediment with low AVS content (1.3  $\mu\text{mol/g}$  dw) and a third sediment which was a 50/50% mixture of the previous ones (AVS = 4.3  $\mu\text{mol/g}$  dry wt). Sediments were spiked with cadmium chloride (from less than 20 to 90,000  $\mu\text{g/g}$  dry sediment = 0.17- 800  $\mu\text{mol/g}$  dw) and allowed to age for seven days. Next to SEM/AVS measurements, total sediment cadmium concentrations and interstitial cadmium concentrations were determined.

Expressed as total cadmium in dry sediment, the  $\text{LC}_{50}\text{s}$  and the observed concentration-response curves differed significantly (i.e. more than an order of magnitude). These concentration-response relationships collapsed into one single concentration-response relationship when the toxicity data were normalized using the test results expressed as cold concentrated acid extracted total cadmium in sediment ( $\mu\text{mol}$ ) per  $\mu\text{mol}$  of AVS

The amphipods  $\text{LC}_{50}\text{s}$  on such an AVS normalized basis were 1.7 to 2.2  $\mu\text{mol Cd}/\mu\text{mol AVS}$  and did not differ significantly ( $p < 0.05$ ) between the three sediments. As such it was clearly demonstrated that cadmium toxicity in sediments is governed by AVS and that the latter could be used for normalization purposes reducing the observed variability from more than one order of magnitude to no difference at all. Furthermore it was observed that if the molar cadmium/AVS ratio was  $< 1$ , no toxicity was predicted and observed, if this ratio was  $> 1$ , interstitial water (IW) cadmium concentrations increased and toxicity occurred, due to the existence of free cadmium in the IW. Based on this study, Di Toro et al. (1992) suggested that (lack of) toxicity could be predicted by the SEM/AVS ratio. Elevated interstitial pore water metal concentrations and toxicity to benthic animals would only occur if  $\text{SEM/AVS} > 1$ .

### Carlson et al., 1991

The results of Di Toro et al (1990) were corroborated with the results of a study conducted by Carlson et al (1991) who investigated cadmium toxicity for the freshwater oligochaete *Lumbriculus variegatus* and the freshwater snail *Helisoma sp.* Three sediments obtained from Pequaway Lake, East river and West Bearskin lake (with initial AVS concentrations of 3.6, 8.8 and 42  $\mu\text{mol/g}$  dry sediment respectively), were collected in the US, and each spiked (4 day aging period) with 5 concentrations of cadmium (measured Cd concentrations ranging from 0.08 to 142  $\mu\text{mol/g}$  dry sediment). The nominal sediment cadmium/AVS ratios were 10, 3, 1, 1/3, 1/10  $\mu\text{mol}/\mu\text{mol}$  respectively. Dissolved and total cadmium in the overlying water, dissolved cadmium in pore water, total cadmium in the sediment, and AVS were measured. Mortality of the worms and snails and internal cadmium concentrations were determined. Water-only tests to assess mortality of the two species were conducted as well.

Mortality responses differed in the three sediments approximately one order of magnitude, based on the total cadmium in the sediments on a dry weight basis. Normalized to the AVS content, the responses were again virtually the same in the different sediments. Pore water cadmium concentrations were significantly elevated when cadmium/AVS ratios exceeded 1 and cadmium concentrations in overlying water exceeded lethal water-only concentrations only with cadmium/AVS  $> 1$ . The maximum whole-body cadmium residue concentrations appeared to increase in a concentration dependent manner at cadmium/AVS concentrations less than 1 for all three test sediments. However, these values were still equal or below the maximum whole-body cadmium concentrations obtained in survivors of the water-only exposures. It should be noted that organisms were not depurated and hence gut contents were measured as well in the “whole-body” cadmium concentrations. The SEM-AVS concept and its relation with bioaccumulation will be further discussed in chapter 4.

Overall, the results showed that cadmium/AVS ratios were predictive of lack of toxicity in both worms and snails and bioaccumulation was not different between sediment exposed and water only organisms.

### Pesch et al., 1995

In this study, the influence of AVS and interstitial water (IW) cadmium (and nickel) on bioavailability and acute toxicity/bioaccumulation (10d) to the sediment-ingesting marine polychaete, *Neanthes arenaceodentata* was

investigated. Field sediments (Ninigret pond, 2  $\mu\text{mol AVS/g dw}$  and Long Island Sound sediment, 18  $\mu\text{mol AVS/g dry wt}$ ) were spiked with Ni or Cd to obtain nominal SEM/AVS ratios of 0, 0.1, 0.3, 1, 3, 10, 30, 100. For the spiked sediments, measured SEM<sub>Cd</sub> concentrations in the sediments ranged from < 0.4 to 570  $\mu\text{mol/g dw}$ . In addition sediment toxicity tests were also conducted with 16 contaminated field sediments from Foundry Cove. In these experiments SEM/AVS ratios ranged between < 0.04 to 125, with SEM<sub>Cd</sub> concentrations (< 0.28-366  $\mu\text{mol/g dry wt}$ ) representing about about 30 to 60 % of SEM<sub>total</sub>. During the experiments AVS, SEM, IW metal concentrations, mortality, burrowing and tissue concentrations of the worms were determined. Water-only experiments were also conducted

All data were normalized to AVS and IW toxic units (IWTU = IW metal concentration/LC50 value of water-only exposure). In all experiments, no significant mortality was observed when SEM/AVS ratios were < 1 and IWTU were < 1. In the cadmium-spiked experiments, when SEM/AVS ratios or IWTUs were > 1, sediments were either lethal to the worms or the worms did not burrow. Metals were accumulated by worms in cadmium-spiked sediments with SEM/AVS ratios < 1, but this phenomenon was only observed in the laboratory spiked sediments and did strangely enough not occur in the field sediments (see also chapter 4 for a more thorough discussion on this subject).

The absence of toxicity to the polychaetes was correctly predicted with the SEM/AVS concept (no toxicity when SEM/AVS < 1). The presence of metal in worms from sediments with SEM/AVS < 1, was suggested to be resulting from release of cadmium from oxidized metal sulfide (as a result of burrowing), uptake of metal from ingested sediment, or adsorption to body surfaces. Some of the sediments with SEM/AVS > 1 were not toxic, and for some of these sediments, IW metal concentrations were better predictors of lack of toxicity. However, vertical profiles of SEM/AVS or IW cadmium were not available and hence it cannot be excluded that higher SEM/AVS concentrations might have existed in the upper part of the sediment, explaining the toxicity of some sediments with an overall SEM/AVS < 1. The fact that worms did not burrow into the sediment when IWTU > 1, was explained as an avoidance to lethal exposure. In conclusion, the results of Pesch et al (1995) support the hypothesis that when SEM/AVS < 1, sediments will not be acutely toxic.

#### Berry et al., 1996

An experiment similar to that by Pesch et al. was conducted with the estuarine amphipod *Ampelisca abdita* with sediments originating from Ninigret pond (AVS = 1.18-2.25  $\mu\text{mol/g dw}$ ) and Long Island Sound (AVS = 9.7-19.9  $\mu\text{mol/g dry wt}$ ) and a mixture of both (AVS = 4.34  $\mu\text{mol/g dw}$ ). Sediments were spiked with cadmium at nominal molar SEM/AVS concentrations of 0, 0.1, 1, 3, 10 and 30. Sediment were equilibrated for 8-10 days prior to testing. SEM<sub>Cd</sub> concentrations ranged from 1.57 to 177  $\mu\text{mol/g dw}$  for LIS sediment and 0.15-24.3  $\mu\text{mol/g dry wt}$  for Ninigret Pond sediment, respectively. The results of the acute toxicity tests confirmed again the usefulness of the SEM-AVS concept in predicting the absence of toxicity. Bioaccumulation was not part of the experimental design.

#### Höss et al., 2001

In this study natural sediment originating from lake Starnberg in Germany was spiked with measured cadmium concentrations ranging from 55 to 6,000  $\text{mg/kg dw}$ . The AVS concentration was 11  $\mu\text{mol/g dw}$  and the initial organic content was 4 %. Spiked sediments were only allowed to age 72 h before testing. Toxicity tests (72 h) were performed with the nematode *Caenorhabditis elegans*. Next to a gradient in cadmium concentrations the organic content of the sediment was increased to 7.3 and 11.7 % by addition of a peat source.

The results of the toxicity tests showed that no effects on the growth of *C. elegans* was observed if sediment concentrations of cadmium were below concentrations of AVS again confirming the SEM/AVS concept for predicting lack of toxicity. At SEM/AVS ratios above one the toxicity in the sediments increased with increasing organic content. According to the authors this was due to the solubilization of cadmium by complexing with dissolved organic matter. It was also suggested that cadmium bound to particulate organic matter (POM) might have been available for the nematodes via dietary assimilation.

#### De Witt et al., 1996 (chronic/marine)

In addition to the short term studies, a full life-cycle chronic study has been conducted with marine organisms. De Witt et al. (1996) exposed newborn marine amphipods, *Leptocheirus plumulosus* to cadmium-spiked estuarine sediments for 28 days under semi-static renewal conditions to determine effects on mortality, growth, and reproduction relative to interstitial water and SEM/AVS normalization. Six cadmium concentrations and a control were tested (with nominal cadmium concentrations in the sediment ranging from 0 to 6,508  $\mu\text{g Cd/g dry wt}$ ,

corresponding nominal Cd/AVS ratios ranging from 0 to 3 and measured  $SEM_{Cd}/AVS$  ratios ranging from 0 to 4.82). Spiked sediments were stored 6 days prior to adding to the exposure chambers. An additional 8 days equilibration time was allowed in the exposure chambers before adding the juvenile amphipods to prevent exposing the amphipods to very high overlying water cadmium concentration released during the initial oxidation of surficial sediments. Interstitial as well as overlying water concentrations were measured during the experiments. Although the sediment characteristics are described (fine grained sediments < 250  $\mu m$ , 3 % total organic carbon, AVS content = 19.3  $\mu mol/g dw$ ) the origin of the sediment is not mentioned.

Significant decrease in average bulk AVS concentration occurred between the time the sediment was spiked with cadmium (19.3  $\mu mol/g dw$ ) and when exposure was initiated (6.5  $\mu mol/g dw$ ). In the exposure chambers a vertical gradient in AVS – caused by oxidation of AVS near the sediment/overlying water interface – was found to be most pronounced after longer incubation periods. AVS concentrations increased with increasing depth and increasing  $SEM_{Cd}/AVS$  ratios. The relative AVS increase with depth was greatest at lower cadmium concentrations. There was an abrupt change in chronic toxicity and interstitial water Cd concentration ( $IW_{Cd}$ ) that occurred between the treatments with  $SEM_{Cd}/AVS$  ratios of 1.55 and 2.23. No significant differences from the control were observed for mortality, growth, and reproduction of *L. plumulosus* in the 4 cadmium treatments at or below  $SEM_{Cd}/AVS$  ratios of 1.55. Moreover,  $IW_{Cd}$  concentrations and overlying water cadmium concentrations were approximately equal (within a factor of 1-4) in the non-lethal treatments ( $SEM_{Cd}/AVS$  ratios < 1.55). Complete mortality was observed in both the treatment with  $SEM_{Cd}/AVS$  ratios of 2.23 and 4.82.

AVS changes in time with increasing depths and increasing  $SEM/AVS$  ratios were probably caused by (1) differences in iron and cadmium sulfide oxidation (iron sulfides oxidize faster than cadmium sulfides, thus the depletion of AVS near the sediment surface was greater in the controls and lower cadmium concentrations), and (2) bioturbation of the test organisms, increasing the transport of oxygen below the sediment/water interface (no bioturbation in the highest concentrations, and hence reduced AVS oxidation rates). The dominant factor was suggested to be the difference in oxidation rates of cadmium and iron sulfide. In the lowest concentrations almost all AVS was iron sulfide, in the higher concentrations almost all AVS was cadmium sulfide and in the intermediate treatments AVS was a combination of cadmium and iron sulfide. Once the iron sulfide in the lower treatments was oxidized, the remaining sulfide was mostly cadmium sulfide, with a slower oxidation rate, explaining the slower AVS oxidation at the end of the experiment. These findings are in accordance with field studies, where AVS concentrations are lowest at the sediment surface, increase with depths to a maximum at the oxic-anoxic boundary (2 to 5 cm depth) and then decline to a relatively constant concentration in deeper sediments. Further, AVS controlled the partitioning of cadmium into interstitial water and thereby determined bioavailability and toxicity.

Overall, the results of this study are consistent with the predictions of cadmium bioavailability in acute tests, i.e. sediments with  $SEM/AVS < 1$  are not toxic; sediments with  $SEM/AVS$  ratios > 1 may be toxic if the  $IW_{Cd}$  exceeds lethal concentrations.

### Hansen et al., 1996 (chronic/marine)

Hansen et al. (1996) followed the effect on colonization of cadmium spiked sediment in a 118 d (July-October 1991) laboratory experiment using a field sediment sampled from central Long Island Sound south of Milford, Connecticut, US (homogenized and defaunated), overflowing with unfiltered seawater from the West Passage of Narragansett Bay, US. The initial AVS concentration was 17.2  $\mu mol/g dw$ . The sediment (mean initial AVS concentration = 17.2  $\mu mol/g dw$ , TOC = 1%) was spiked with cadmium chloride, to nominal  $SEM_{Cd}/AVS$  ratios of 0, 0.1, 0.8 and 3.0  $\mu mol/\mu mol$  (193-5,800  $\mu g$  cadmium/g dry wt). Sediments were allowed to age 26 days prior to testing. Different treatments are denoted control, 0.1x, 0.8x and 3.0x treatment. Aquaria were sampled on day 14, 28, 56 and 117 for AVS, SEM,  $IW_{Cd}$ , and on day 80 and 118 for biology (numbers, abundance and composition of species/communities).

Measured  $SEM_{Cd}$  and AVS concentrations indicated that the exposure was relatively constant in time. AVS and  $SEM_{Cd}$  concentrations, however, varied with sediment depth. AVS decreased in the upper sediment layers in all treatments. More AVS was lost in the lower  $SEM_{Cd}$  treatments.  $SEM_{Cd}/AVS$  ratios remained stable, close to the nominal values at sediment depths greater than 2.4 cm, but increased greatly in surficial sediments. Measured  $SEM_{Cd}/AVS$  were always lower than 1 in the control and 0.1x treatment, frequently above 1 in the surficial sediment in the 0.8x treatment and always above 1 in the 3.0x treatment. Concentrations of cadmium measured in interstitial water were consistent with sulfide binding. They were very low in the control and 0.1x treatment, reached levels sufficiently high to be acutely toxic to the most sensitive species in the 0.8 treatment (48-58  $\mu g/L$  on average in the bottom and surface sediment, corresponding to  $SEM_{Cd}/AVS$  ratios being frequently > 1 in the superficial sediments of this treatment), and were up to 174,000  $\mu g/L$  in the 3.0x treatment. There were cadmium-related differences in timing of appearance, abundance and species of organisms found in each treatment except for the 0.1 treatment.

Cluster analysis revealed three groups of species (control and 0.1x treatment were similar). Species richness and abundance decreased as the SEM/AVS ratios increased in the other treatments (0.8 and 3.0 treatment).

The loss of AVS in the surficial sediments was likely due to oxidation, principally of iron sulfide. The oxidation was likely associated with passive oxygen diffusion and not biologically driven. Winter AVS concentrations in surficial sediments decrease as a result of AVS being readily oxidized in cold months. The more limited loss of AVS in the 3.0x treatment was probably due to the lower oxidation rate of cadmium sulfide. Loss of SEM<sub>Cd</sub> was essentially confined to the upper 1.2 cm of the sediment. Vertical profiles of measured SEM<sub>Cd</sub>/AVS ratios were consistent with the observed oxidation of AVS in surficial sediments as tempered by losses of cadmium (SEM<sub>Cd</sub>). The significant increase of SEM<sub>Cd</sub>/AVS ratios in surficial sediments was due to the AVS losses exceeding SEM<sub>Cd</sub> losses. Although average SEM<sub>Cd</sub>/AVS ratios were 0.6 on average in the 0.8x treatment, they exceeded 1 in the upper sediment and molar concentrations of cadmium in the IW frequently exceeded those that in water-only tests are known to be acutely toxic to sensitive species. This explains the at first sight contradicting observation of finding toxic effects at SEM/AVS ratios < 1. In the 3.0x treatment these concentrations were always greatly exceeded.

This study showed (1) that the observed biological responses were consistent with SEM<sub>Cd</sub>/AVS ratios in surficial sediments and interstitial water cadmium concentrations; (2) that predictions of the toxicological significance of metals in laboratory and field sediments must ideally consider vertical profiles of measured SEM and AVS, IW metals concentrations, and the potential for release of non-available metals as a result of oxidation of AVS, as part of the normal seasonal sulfide cycles and sediment bioturbation.

#### Hare et al., 1994 (chronic/marine)

A natural sediment (Lake Tantaré, Canada) was sampled below the top 1-10 cm and mixed well. The sediment contained 0.5  $\mu\text{mol AVS/g}_{\text{dw}}$  and the Cd:AVS molar ratio  $\sim 0.05$  in the control. The sediments were spiked with Cd(NO<sub>3</sub>)<sub>2</sub> (0.05-0.1-0.5-2-10 Cd:AVS molar ratio, 12 replicates). The spiked sediments were poured into rectangular plastic containers (volume 8L, surface area 0.07 m<sup>2</sup>). The containers were closed and replaced at the original collection site. Water characteristics: pH 5.3-5.6, H 3 mg CaCO<sub>3</sub>/L, 4-6 °C. The mean total abundance for all taxa in the test trays was not significantly related to Cd exposure. Taken individually (at species level), the abundances of most species also did not appear to be related to exposure up to the highest Cd exposure level (563  $\mu\text{g Cd g}^{-1}_{\text{dw}}$ ). Only the number of *Chironomus (salinarius gp)* sp., which is one of the most abundant *Chironomidae* species, was strongly reduced at 563  $\mu\text{g Cd g}^{-1}_{\text{dw}}$ . Larvae of this species burrow deep in the sediment and have their guts filled with sediment, indicating a high exposure via sediment intake. The NOEC was observed at 115 mg/kg (i.e. at SEM<sub>Cd</sub>/AVS=2) and the LOEC at 563 mg/kg (SEM<sub>Cd</sub>/AVS=10) illustrating the lack of effects below bSEM/AVS=1.

#### Boothman et al., 2001 (chronic/marine)

A 4 months full size field recolonisation study was conducted by Boothman et al. (2001) in Narragansett bay. Sediment from Narragansett Bay, US, was sieved, homogenized and frozen (for defaunation). Sediments (77 % silt/23 % sand, 1.2 % organic carbon and initial AVS concentration of 9  $\mu\text{mol/g dw}$ ) were spiked with equimolar quantities of cadmium, copper, lead, nickel and zinc. Nominal total metal/AVS ratios were 0.1, 0.8 and 3.0. Different treatments are denoted control, 0.1x, 0.8x and 3.0x. Trays filled with defaunated control or metal-spiked sediment were placed again in Narragansett Bay. Apart from SEM, AVS and interstitial water metal concentrations (day 0, 15, 27, 56 and 119 in sections at different depths), recolonization by biota was determined (day 119).

AVS concentration in the surface layer (0-3 cm) decreased significantly in time, except in the 0.8x and 3.0x treatments. In the high metal dose experiment, SEM decreased. In the subsurface layer (6-10 cm) no decrease of AVS with time was detected. Also SEM/AVS decreased with time in the surface sediment layer. On day 119 of the experiment, sediment cores from the different treatments were collected and sectioned in 0.6 cm intervals to allow profiles of metals and AVS to be determined with finer resolution. While the AVS concentrations usually decreased in the top 2 cm (except in the 3.0x series), AVS typically increased at all sediment depths below about 2 cm in all treatments. Unlike sulfides, the profiles of SEM showed little change in cores below 2-3 cm. Much like AVS, however, metal concentrations decreased substantially in surface sediments down to almost 3 cm depth. The core profiles finally showed that AVS exceeded SEM throughout the sediment column in all but the 3.0x treatments. In the highest metal treatment, SEM/AVS > 1 were found particularly in the deeper layers (below 3 cm), where SEM exceeded AVS by 10  $\mu\text{mol/g}$  or more. In sediments less than 2 cm deep, though, excess metals (SEM – AVS) were less than 4  $\mu\text{mol/g}$  in all samples and less than zero in some. Concentrations of metals in the IW were undetectable when SEM/AVS < 1 and were enhanced when SEM/AVS > 1, with the least soluble sulfides always below detection limits. As a consequence, cadmium (CdS being little soluble) was only measured in the 3.0x treatment, but

significantly decreased in that treatment in time. After 119 days exposure faunal assemblages were similar to those in the control.

AVS did not significantly decrease in time in the 0.8x and 3.0x treatments because of the formation of copper, zinc, nickel, lead and cadmium sulfides which oxidize more slowly than FeS. Lower concentrations of AVS in surface sediments reflect processes in which oxygenated seawater mixes with anoxic IW and oxidizes the sulfides. Further, possible export of experimental sediments and import of ambient sediments may have occurred. Adding metals decreased the concentrations of AVS, because nickel and copper sulfides are not easily extractable and thus reduce the amount of AVS. AVS concentrations above the initial concentration in the control and 0.1x, are most likely reflecting microbial production of sulfide because of warmer summer temperatures and anoxic conditions in the deeper sediments. The decrease in SEM concentrations in surface sections, may be attributed to diffusion from pore water to overlying water and active transport through bioturbation and resuspension of sediments. SEM/AVS ratios changing from  $> 1$  to  $< 1$  for the 0.8x at day 56, are most likely due to sulfides produced in the deeper sediments. Based on SEM/AVS data, it was predicted that metals could be present in interstitial waters of the 0.8x and 3.0x treatments. Metals were measured in the interstitial water of the 3.0x treatment and decreased with time, with cadmium concentrations exceeding USEPA marine chronic water quality criteria by one to two orders of magnitude for the first 56 days.

Lack of biological response was related to vertical distributions of AVS and SEM, with AVS exceeding SEM even in the highest concentration in the surficial sediment sections. Because benthic species initially colonize sediments at the seawater interface, conditions at the interface would control colonization and effects on benthic organisms more than the deeper sediment conditions. Since metals are released from the uppermost sediment layer and readily washed away, this may explain the lack of biological effects.

In conclusion, colonization by benthic organisms was related more to SEM/AVS in the upper 1 to 2 cm of the sediment than to concentrations of metals in interstitial water at depths of 1 to 3 cm (this latter being an integrated, average concentration of the 1 to 3 cm layers). The results of this study clearly show that the conditions in the field may differ from those conditions mimicked in the laboratory. For example in the laboratory recolonization study by Hansen et al (1996) using almost the same test design a significant biological response was noted in the 0.8x and 3.0x treatments which could be explained due to the significant increase of  $SEM_{Cd}/AVS$  ratios in surficial sediments (AVS losses exceeding  $SEM_{Cd}$  losses). While the results from Boothman et al (2001) suggest that when metals-spiked sediments are placed in natural dynamic environments, field conditions do not allow high concentrations of excess metals to exist in the surficial sediments for long periods, most likely due to physical resuspension releasing metals from pore water into overlying waters. This emphasizes again the merit of using fine-scale vertical gradients and seasonal variations when using AVS and SEM measurements to assess the bioavailability of metals under natural conditions.

#### Hare et al., 2001 (chronic/freshwater)

Hare et al (2001) reported an 11 months field colonization study (June 1994-May 1995) with cadmium spiked sediments deployed in trays in lake Laflamme (Canada) investigating the ability of AVS to predict cadmium bioaccumulation and effects. Sediments of the lake were defaunated and mixed, cadmium was added (nominal concentrations of 0.0, 0.2, 0.4, 0.8, 1.6 and 3.2  $\mu\text{mol/g dw}$ ) and trays were placed on the bottom of the lake. Total sediment cadmium concentrations, AVS, SEM, interstitial cadmium concentrations,  $\text{H}_2\text{S}$ ,  $\text{SO}_4$  and pH were determined at the end of the experiment. Pore water and overlying water were sampled for cadmium determination after 2 and 11 months, animals and sediments after 11 months. A smaller experiment was also set up to determine residence time and cadmium content of the invertebrates in the test containers (sampled at regular intervals up to 28 days in autumn and 56 days in spring).

The AVS concentration in the control at the end of the study were low (0.9  $\mu\text{mol/g dw}$ ) Near-surfaces losses of AVS and increasing AVS concentrations with increasing cadmium concentrations were noted (1-2.8  $\mu\text{mol/g dw}$ ) When all trace metals were added (not only cadmium), average SEM/AVS were  $> 1$  in all treatments (ratios ranging from 1.16 to 1.47). Little cadmium was measured in the IW in all but the highest treatment levels. For the biology, an overall lack of toxic effects was observed. Cadmium accumulation by invertebrates, however, was observed and was mainly related to the uptake from cadmium by the overlying water route. As such the authors concluded that the protection of benthic communities from metal pollution should not only be focused on the sediment compartment but should also pay attention to the water column compartment which in this study contributes significantly to the observed bioaccumulation.

The decrease in AVS concentration in the upper sediment layers is likely due to sulfide oxidation. The AVS burden for a given cadmium treatment increased progressively over time, largely because of the downward transport and reduction of  $\text{SO}_4$  and the fixation of the resulting sulfide with the added cadmium (with more cadmium available in

the higher treatment levels) which is less susceptible towards oxidation. Although SEM/AVS was  $> 1$  in all treatments, IW cadmium concentrations were only elevated in the highest treatment level. This is explained by the fact that other sulfides than CdS are more soluble. In other words, cadmium is not released as long as more soluble sulfides can be released (in this research study zinc). The lack of toxic effects on biota at SEM/AVS ratios larger than one can be explained by the fact that interstitial water and sediment cadmium concentrations were low in the upper sediment layers. Hence, the AVS model was effective in predicting the cadmium pore water concentrations and the lack of toxicity. The observed bioaccumulation does not mean that the SEM-AVS concept is flawed but merely reflects the importance of waterborne cadmium as exposure route to benthic organism.

## Annex 2 EU dataset on SEM/AVS

The information of this annex is extracted from the report : Probabilistic assessment of cadmium bioavailability in sediments, as prepared by EURAS (Vangheluwe M, Heijerick D. and F. Verdonck, 2004); for the annexes the reader is referred to the original report.

### 3.1 Description and assessment of data sets included in the database

#### 3.1.1 Introduction

Data on AVS and SEM concentrations were compiled from peer reviewed literature and governmental reports by Vangheluwe et al (2003). In addition, the initially identified Flemish Sediment Database was, in close collaboration with the Flemish Environment Agency (FEA), extended with 149 new entries during the course of that project. European data on SEM/AVS concentrations are limited. Most data are available for sediments in the Flemish region (Belgium: Flemish Sediment Database) and the Netherlands. SEM/AVS concentrations were also available for a suite of 10 reference sites distributed over Europe (principally Italy, Belgium, the Netherlands, Germany, Sweden and the UK) measured in the framework of the EUROECOLE (2001) project.

#### 3.1.2 Detailed description of the data sets

As a prerequisite for a data set to be included in the analysis, AVS concentration and individual SEM data had to be reported and data should be representative for a regional exposure. For some data sets, additional information on the fraction of organic carbon (fOC) in the sediment and/or corresponding toxicity was available. The details of the different data sets are provided in Table 2 and annex 1 of the report prepared by EURAS, 2004.

**Table 2:** Overview compiled SEM/AVS data sets for European freshwater sediments

Country	Sampling location	Number of sampling points	Reference
Flemish Sediment Database 1	Dommel, IJzer + small riverines	51	De Cooman et al, 1995
Flemish Sediment Database 2		149	Vangheluwe et al, 2003
Belgium	Bihain (river)	1	Euroecole, 2001
Belgium	Somerain (river)	2	Euroecole, 2001
UK	Mole (river)	1	Euroecole, 2001
Germany	Rhine (river)	1	Euroecole, 2001
Germany	Schmallenberg (pond)	1	Euroecole, 2001
Hungary	Tisza (river)	7	Lengyel et al, 2002
Hungary	Szamos (river)	3	Lengyel et al, 2002
Italy	Segrino (Lake)	1	Euroecole, 2001
The Netherlands	Marken (lake)	1	Euroecole, 2001

The Netherlands	Ankeveen (river)	2	Euroecole, 2001
The Netherlands	Meuse (river)	4	Van Den Berg et al, 1998
The Netherlands	Ketelmeer (lake)	5	Van Den Berg et al 1997 and 2001
The Netherlands	Leeghwaterplas (lake)	1	Van Den Berg et al, 2001
The Netherlands	Botlek (lake)	1	Van Den Berg et al, 2001
The Netherlands	Nieuwersluis	1	Van Den Hoop et al, 1997
The Netherlands	Oostvaarders Plassen	1	Van Den Hoop et al, 1997
The Netherlands	Schoonrewoerdse Wiel	1	Van Den Hoop et al, 1997
The Netherlands	Almere Waterwijk	1	Van Den Hoop et al, 1997
The Netherlands	Kromme Rijn (river)	1	Van Den Hoop et al, 1997
Sweden	Skarsjön (lake)	1	Euroecole, 2001
Sweden	Mälaren (lake)	3	Wiklund and Sundelin, 2002

The level of detail in which the SEM/AVS data are reported is not always the same. Sometimes only the total SEM concentration is given making it impossible to quantify the cadmium specific contribution (this is the case for Almere Waterwijk and Kromme Rijn river). In other cases SEM data are not representative for a regional scenario since they reflect unusual conditions. For example, the data for Hungary are the results of a sampling campaign after a heavy metal sludge spill into the river Tisza in March 2000 resulting in very high levels of heavy metal loaded into the sediment of these riverine ecosystems. After this prescreening, the overall database, consists of 226 data points for which a complete set of data are available.

Most data are available for the Flemish region from an ongoing sediment monitoring program in which the Flemish Environment Agency is measuring sediment quality on a routine basis with the TRIAD approach. The Flemish Sediment Database has been developed by the Flemish Environment Agency in close collaboration with the Ministry of Environment and Infrastructure (AMINAL division water and AWZ) (De Cooman et al, 1995, De Cooman et al., 1998, De Cooman et al 1999a & b, De Deckere et al, 2000). The database covers sediments originating from both navigable and non-navigable watercourses (sampled over the period 1993-2002), in which data on synoptic measurements of chemical concentrations, *in situ* biological community assessments and sediment toxicity testing are provided. The monitoring database is updated every year with 150 new entries. A detailed description of the parameters (Table 3) is outside the scope of this report but can be found in the references mentioned above.



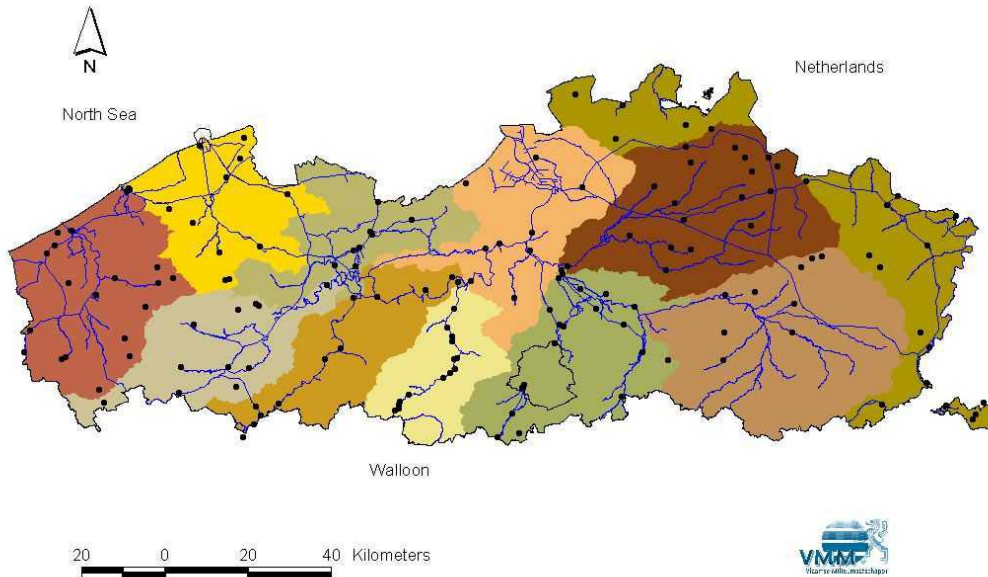
**Table 3: Overview of the parameters measured in the framework of the TRIAD approach**

Physico-chemical component	Ecotoxicological component	Biological component
1. particle size	1. <i>Raphidocelis subcapitata</i> (pore water)	1. biotic sediment index (BSI)
2. percent organic matter	2. <i>Thamnocephalus platyurus</i> (pore water)	
3. arsenic (As)	3. <i>Hyalella azteca</i> (bulk sediment)	
4. cadmium (Cd)		
5. chromium (Cr)		
6. copper (Cu)		
7. mercury (Hg)		
8. nickel (Ni)		
9. lead (Pb)		
10. zinc (Zn)		
11. apolar hydrocarbons (APHC)		
12. extractable organohalogenes (EOX)		
13. sum organochlorine pesticides (SOCP's)		
14. 7 PCBs		
15. 6 PAHs (Borneff)		
16. SEM/AVS (only measured in the framework of this study)		

Chemical analysis is restricted to the bulk sediment. The SEM/AVS analysis was performed according to the methodology as described by Allen (1993) on a sediment aliquot taken from the bulk sediment.

Data on SEM and AVS concentrations in Flanders have already been measured on 51 sediments in 1995. In order to obtain a more complete picture of the spatial heterogeneity of AVS and SEM concentrations in Flanders collaboration between EURAS and the Flemish Environment Agency has been established (Vangheluwe et al, 2003). During an extensive sampling campaign (149 sediments) in which the TRIAD approach is deployed extra samples for SEM/AVS measurements were taken. The sample campaign was initiated in March 2002 and was completed by the end of May 2002. It should be noted that since the samples were taken in the spring, seasonal issues are avoided. Furthermore, from literature it can be expected that the AVS levels measured during a winter/spring sampling campaign represents a worst case scenario (i.e. lowest AVS levels).

In the selection of the sediments originating from navigable and unnavigable watercourses in Flanders care was taken that the 11 river basins in Flanders were sampled. As such the sediments represent a gradient of contamination and grain size distributions varying from sandy to silt sediments. As shown in section 3.2, the few data available for other European countries seem to indicate that the Flemish database provides a good coverage of SEM/AVS/FOC concentrations found in these sediments. The different sites of the 2002 campaign are visualized in **Figure 1**.



**Figure 1:** Overview of the 149 sampling sites in Flanders (Belgium) analysed during March-June 2002 (by courtesy of FEA)

### 3.1.3 Data treatment

#### 3.1.3.1 Dealing with the multiple metals issue

In applying the SEM-AVS model for a specific metal, such as cadmium, it has to be taken into consideration that  $\Sigma\text{SEM}$  represents the sum of different metals acting in a competitive manner when binding to AVS. For the current database, cadmium represents 0.01-7 % of the total SEM. Acknowledging the existence of competitive displacement kinetics between various metals and reduced sulfur, the SEM-AVS model can be made metal specific. The procedure that is used is to assign the AVS pool to the metals in the sequence of their sulfide solubility products. Ranked from the lowest to the highest solubility product the following sequence is observed:  $\text{SEM}_{\text{Cu}}$ ,  $\text{SEM}_{\text{Pb}}$ ,  $\text{SEM}_{\text{Cd}}$ ,  $\text{SEM}_{\text{Zn}}$  and  $\text{SEM}_{\text{Ni}}$ . Meaning copper has the highest affinity for AVS, followed by lead, cadmium etc until the AVS is exhausted. The remaining SEM is that amount present in excess of the AVS. Mercury and silver have lower sulfide solubilities than cadmium, but their molar concentrations are always sufficiently low as to not influence the calculations.

To demonstrate, let  $\Delta \{\text{SEM}_i\}$  be the excess SEM for each of the  $i^{\text{th}}$  metals. The least soluble metal sulfide (of the five metals considered above) is copper sulfide. Thus, if the simultaneously extracted copper is less than the AVS ( $\{\text{SEM}_{\text{Cu}}\} < \{\text{AVS}\}$ ), then essentially all of it must be present as copper sulfide with no additional  $\text{SEM}_{\text{Cu}}$  present, such that the difference between  $\text{SEM}_{\text{total}}$  and  $\text{SEM}_{\text{Cu}} = \Delta \{\text{SEM}_{\text{Cu}}\} = 0$ . The remaining AVS binding pool is  $\Delta \{\text{AVS}\} = \{\text{AVS}\} - \{\text{SEM}_{\text{Cu}}\}$ . This computation is repeated next for lead and cadmium because these are the next least soluble sulfides. Just suppose as an example that unlike copper and lead the simultaneously extracted cadmium is not less than the remaining AVS  $= \Delta \{\text{AVS}\} = \{\text{AVS}\} - \{\text{SEM}_{\text{Cu}}\} - \{\text{SEM}_{\text{Pb}}\}$ . Hence, only a portion of the simultaneously extracted cadmium is present as cadmium sulfide and the remainder is present as excess SEM. Because the AVS has been

exhausted by the cadmium in this example, the remaining two metals, zinc and nickel, would all be present as excess SEM.

E.g.

Suppose 1 mole of AVS is present, 0.3 moles of SEM<sub>Cu</sub>, 0.4 moles of SEM<sub>Pb</sub>, 0.5 moles of SEM<sub>Cd</sub>, 0.2 moles of SEM<sub>Zn</sub> and 0.1 moles of SEM<sub>Ni</sub>. Then  $\Delta \{SEM_{Cu}\} = \Delta \{SEM_{Pb}\} = 0$ . The remaining AVS =  $\Delta \{AVS\} = \{AVS\} - \{SEM_{Cu}\} - \{SEM_{Pb}\} = 1 - 0.3 - 0.4 = 0.3$  moles. Since the  $\{SEM_{Cd}\}$  exceeds the remaining AVS,  $\Delta \{SEM_{Cd}\} = \{SEM_{Cd}\} - \Delta \{AVS\} = 0.5 - 0.3 = 0.2$  moles. Because all AVS has been exhausted  $\Delta \{SEM_{Zn}\} = \{SEM_{Zn}\} = 0.2$  moles and  $\Delta \{SEM_{Ni}\} = \{SEM_{Ni}\} = 0.1$  moles.

To summarise:

In the case of cadmium, the excess SEM<sub>Cd</sub> (μmol/gDW) was calculated as follows:

$$\text{Excess SEM}_{Cd} = SEM_{Cd} - \Delta AVS_{Cd}$$

For cadmium

$$\Delta AVS_{Cd} = AVS_{tot} - (SEM_{Cu} + SEM_{Pb}) \quad (\text{if AVS exhausted} = 0)$$

### 3.1.3.2 Elaboration of Cumulative Distribution Functions

From the compiled data set frequency distributions of ambient AVS and SEM<sub>Cd</sub> exposure concentrations in the sediments were elaborated in order to derive the bioavailable predicted environmental concentration (PEC) for the sediment compartment.

Using the statistical package @Risk (Pallisade Decision Tools) the parametric or non-parametric distribution that best fits the input data was selected. Non-parametric distributions were preferred when sufficient data points (e.g. 100-150 measurements or more) were available. For data sets with fewer observations a parametric distribution was selected to fit the data. Most often frequency distributions of exposure concentrations in the environment are distributed according to the lognormal model (Klaine et al., 1996; Solomon et al., 1996; Solomon and Chappel, 1998). The goodness-of-fit tests that are used for screening the selected distribution are Chi-Square, Kolgomorov-Smirnov and Anderson-Darling (Cullen & Frey, 1999). The latter test mainly focuses on the goodness-of-fit in the tails of the distribution, and is therefore the most appropriate test when e.g. 90<sup>th</sup> or 10<sup>th</sup> percentiles have to be considered.

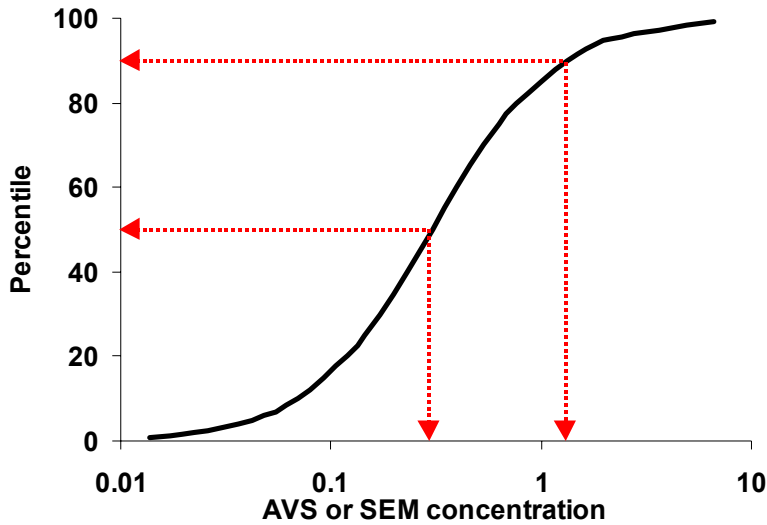
Table 4 gives an overview of the selected distributions for the different data sets. Data of The Netherlands were log-transformed before fitting to a distribution.

**Table 4:** Selected parametric and non-parametric distributions for determination of 10<sup>th</sup>, 50<sup>th</sup> and 90<sup>th</sup> percentiles and performing Monte-Carlo analysis (see chapter 4).

	Flanders	The Netherlands	Aggregated data
AVS	Non-parametric	log-Weibull	Non-parametric
ΣSEM	Non-parametric	log-Triangular	Non-parametric
ΔAVS <sub>Cd</sub>	Non-parametric	/	Non-parametric
SEM <sub>Cd</sub>	Non-parametric	Log-Normal	Non-parametric
SEM <sub>Cd</sub> - ΔAVS <sub>Cd</sub>	Non-parametric	/	Non-parametric

fOC	Non-parametric	/	Non-parametric
$(SEM_{Cd} - \Delta AVS_{Cd})/fOC$	Non-parametric	/	Non-parametric

From the produced non-parametric or parametric distributions it is possible to assign probabilities to the likelihood that a measure will exceed a certain value. The principle of deriving a 90<sup>th</sup> percentile is illustrated in Figure 2.



**Figure 2:** PEC derivation as 90<sup>th</sup> percentile

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<sup>4</sup> The 90<sup>th</sup> percentile is chosen because it represents a reasonable extreme case on the overall distribution. Values beyond the the 90<sup>th</sup> percentile tend to lie on the tails of the distributions are frequently driven by a very few extreme values that may be outliers. Use of 90<sup>th</sup> percentile for assessment of given distribution is consistent with the approach used in the zinc risk assessment and the TGD.

## 3.2 Results exposure assessment Acid Volatile Sulfides (AVS), Simultaneous Extracted Metals (ΣSEM) and organic carbon (fOC)

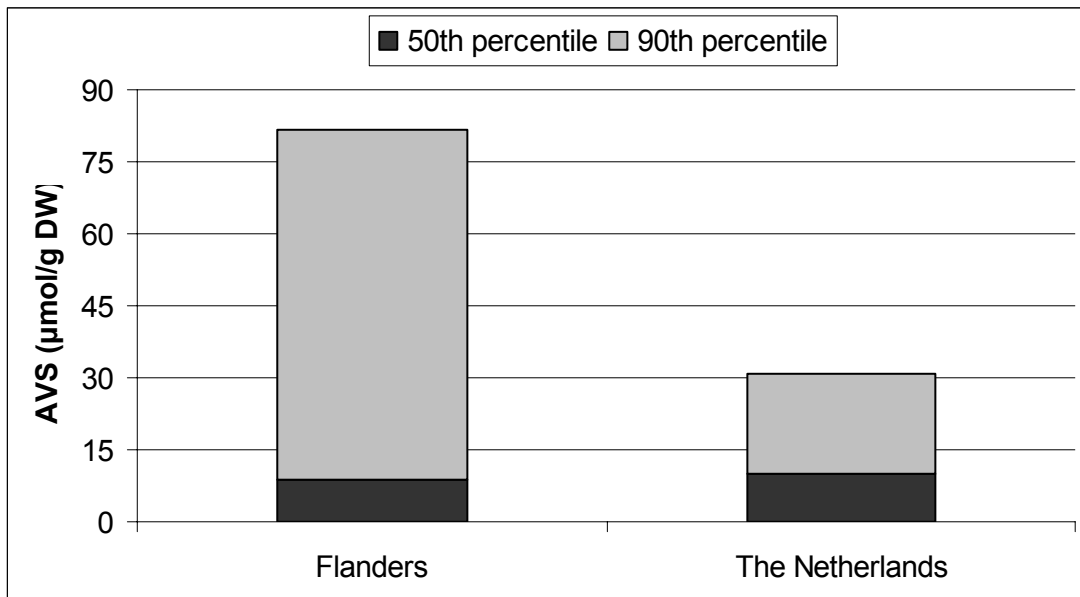
### 3.2.1 Introduction

The results of the detailed data analysis on the different databases (Flanders: 200 data points; The Netherlands: 16 (freshwater) and the rest of Europe: 10 data points) are presented in annex 2 of the report prepared by EURAS, 2004. In chapter 4 the results of a detailed analysis on the aggregated freshwater data (226 data points representative for the whole of Europe) and Flanders are presented and discussed.

### 3.2.2 AVS concentrations in European sediments

#### 3.2.2.1 AVS concentrations for Belgium and the Netherlands

Data on AVS concentrations in the freshwater sediments of the Flemish region (Belgium) and the Netherlands were obtained for Flanders from the Flemish sediment database (n = 200) and from governmental reports and peer reviewed literature for the Dutch situation (n= 16 for freshwater). An overview of the 50<sup>th</sup> and 90<sup>th</sup> percentile AVS concentrations in sediments of Flanders (Belgium) and the Netherlands is presented in figure 3. The full databases and the selected cumulative distributions are given in Annex 1 and 2 and shown in figure 4.



**Figure 3:** Ambient AVS concentrations (50<sup>th</sup> and 90<sup>th</sup> percentiles expressed as  $\mu\text{mol/gDW}$  in sediments of Flanders (Belgium) and the Netherlands.

The median and 90<sup>th</sup> percentile values of the separate freshwater databases are respectively 8.8 and 81.5  $\mu\text{mol/gDW}$  for Flanders and 9.8 and 30.9  $\mu\text{mol/gDW}$  for the Netherlands.

#### 3.2.2.2 AVS data for other European countries

Few data were available on the AVS concentrations in the other European countries. The sampling

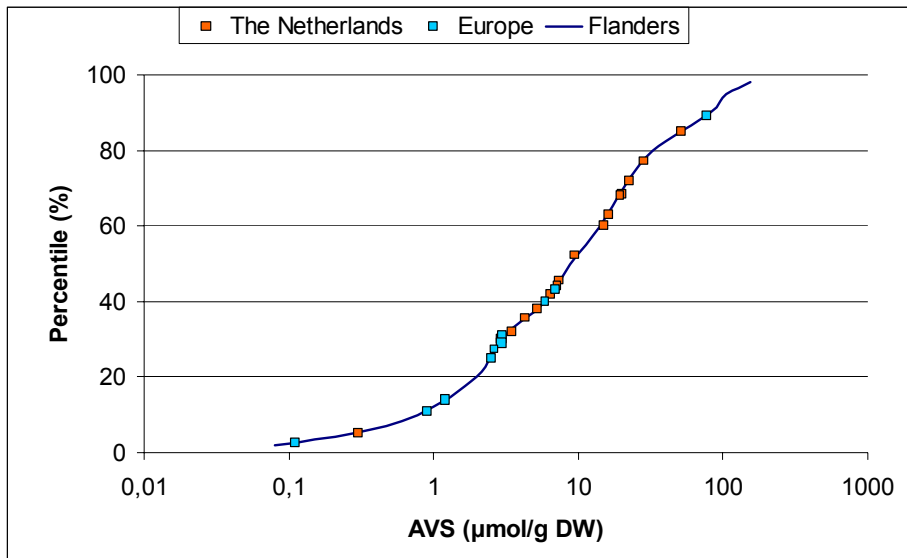
campaign aimed at the sampling of water and sediments from European reference sites, characterized by their negligible/limited anthropogenic influence and a wide variety in water physico-chemistry. A summary of the data is presented in table 5.

**Table 5:** Measured AVS concentrations in European freshwater sediments

Country	Sampling location	Sampling date	AVS ( $\mu\text{mol/gDW}$ )
Belgium	Bihain (river)	11-2000	3.0
		04-2001	3.5
Belgium	Somerein (river)	11-2000	40.0
		04-2001	2.5
England	Mole (river)	05-2001	1.2
Germany	Rhine (river)	04-2001	2.9
Italy	Segrino (Lake)	05-2001	78
Germany	Schmallenberg (pond)	11-2000	7
The Netherlands	Marken (lake)	11-2000	0.3
The Netherlands	Ankeveen (river)	11-2000	25.8
		05-2001	4.3
Sweden	Skarsjön (lake)	11-2000	6

Source:EUROECOLE (2001)

AVS concentrations for the different European reference sites varied between 0.3 and 78  $\mu\text{mol/gDW}$ . These observations are in concordance with the overall freshwater data set ( $n = 200$ ) compiled for Flanders where a median AVS concentration of 8.8  $\mu\text{mol/gDW}$  and a 90<sup>th</sup> percentile of 81.5  $\mu\text{mol/gDW}$  could be derived. In figure 4, the data for the other European countries are plotted on the CDF derived for the Flemish data set (red squares). From the plot it is clear that the Flemish database provides a good coverage of the other European countries for which AVS data are available.

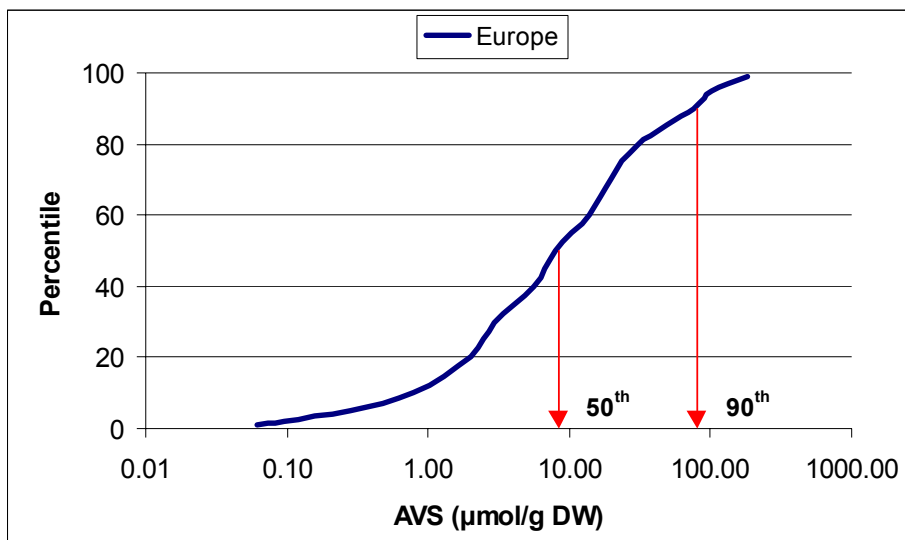


**Figure 4:** Cumulative Frequency distribution of AVS concentrations in sediments of Flanders (Belgium) full line, the Netherlands (red squares) and other European countries (blue squares)

It should be noted that Figure 4 also contains European sediments where AVS concentrations were measured in November (see Table 5). For most of the Dutch data it was not indicated when samples have been taken. Sediments sampled in Lake Ketel (NL) by Van Den Berg et al. (2001) were taken in July-August. Meuse sediments (Van Den Berg, 1998) were sampled in June.

### 3.2.2.3 Overall AVS frequency distribution for Europe

All data have been aggregated together in order to elaborate the AVS frequency distribution representative for the whole of Europe (it should be noted however that the overall data set is of course influenced by the Flemish data (Figure 5). Based on the overall freshwater data set (data from Flanders (n = 200), the Netherlands (n =16) and other European reference sites (n=10)) a median AVS concentration of 8.05 µmol/gDW and a 90<sup>th</sup> percentile of 75.5 µmol/gDW can be calculated.

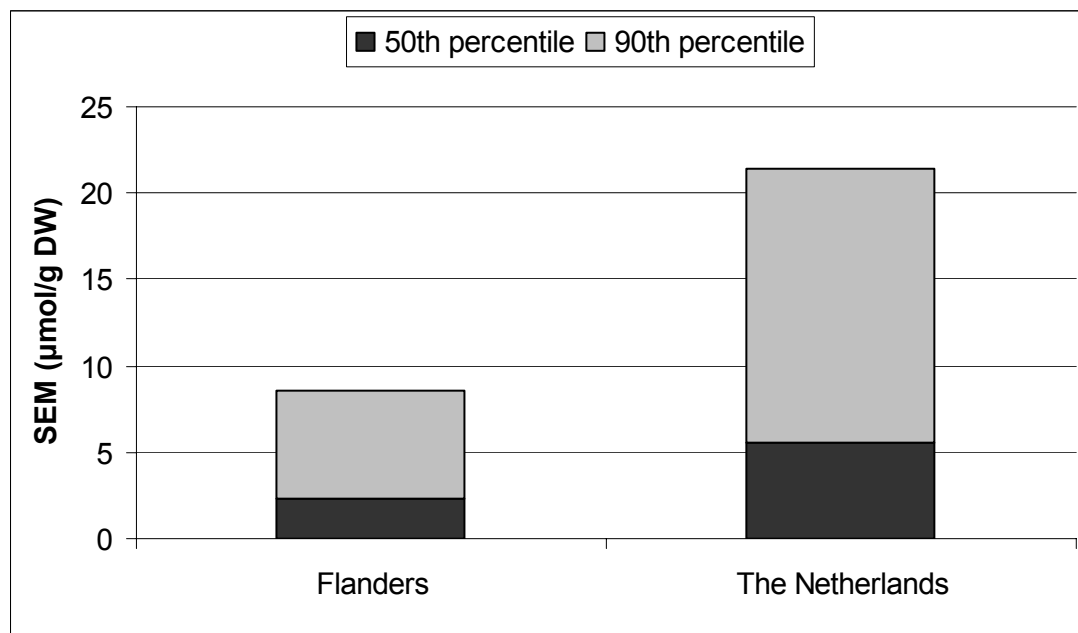


**Figure 5:** Cumulative Frequency distribution (non-parametric) of AVS concentrations (µmol/gDW) in European freshwater sediments.

### 3.2.3 $\Sigma$ SEM concentrations in European sediments

#### 3.2.3.1 $\Sigma$ SEM concentrations for Belgium and the Netherlands

An overview of the cumulative frequency distributions of  $\Sigma$ SEM concentrations in sediments of Flanders (Belgium) and the Netherlands is presented in Figure 6.



**Figure 6:** Ambient  $\Sigma$ SEM concentrations (50<sup>th</sup> and 90<sup>th</sup> percentiles expressed as µmol/gDW) in sediments of Flanders (Belgium) and the Netherlands)



A difference can be observed between the Flemish and Dutch database with a 50<sup>th</sup> percentile SEM values of 2.3 and 5.6  $\mu\text{mol/gDW}$  and 90<sup>th</sup> percentile SEM values of 8.5 and 21.4  $\mu\text{mol/gDW}$  for Flanders (n = 200), and the Netherlands (n = 16), respectively.

The observed difference between the Flemish and Dutch data set are mainly due to the choice of distribution function selected to best fit the observed monitoring data. Due to the restricted size of the Dutch database (n = 16) a parametric function (log-Triangular) has been selected to represent the data points. This distribution tends to overestimate the higher percentiles. The lower values can be seen to be in much closer agreement with the observed data. The min-max range of the measured SEM<sub>total</sub> data for the Netherlands is 0.18  $\mu\text{mol/gDW}$ -17.1  $\mu\text{mol/gDW}$ . For the Flemish data set enough data points were available to use a non-parametric distribution, which best represents the monitored data.

### 3.2.3.2 $\Sigma$ SEM concentrations for other European reference sites

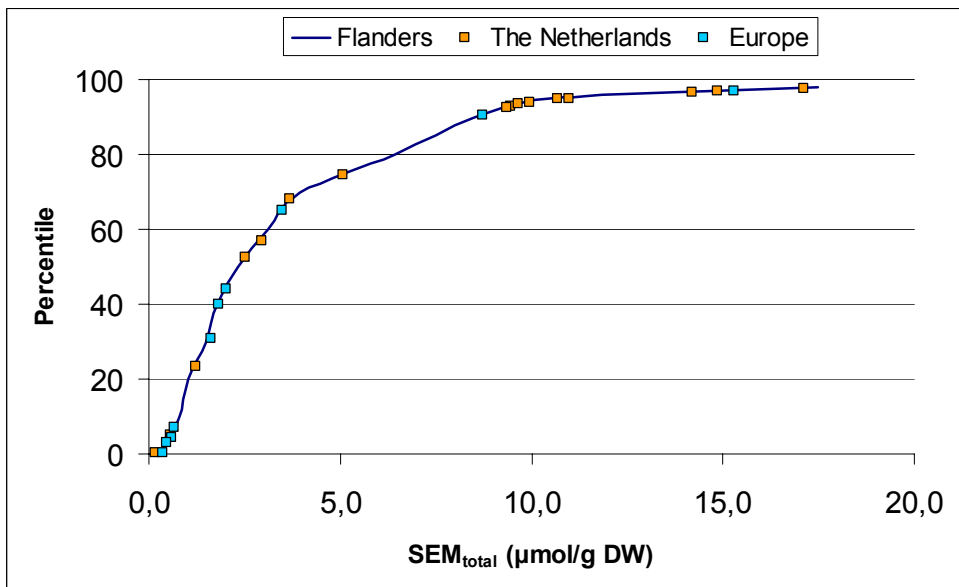
A summary of some of the available data on the  $\Sigma$ SEM concentrations in the other European countries (European reference sites) is presented in table 6.

**Table 6:** Measured SEM concentrations in European freshwater sediments

Country	Sampling location	Sampling date	$\Sigma$ SEM ( $\mu\text{mol/gDW}$ )
Belgium	Bihain (river)	11-2000	0.65
		04-2001	0.5
Belgium	Somerein (river)	11-2000	1.63
		04-2001	1.62
England	Mole (river)	05-2001	0.35
Germany	Rhine (river)	04-2001	0.59
Italy	Segrino (Lake)	05-2001	2.01
Germany	Schmallenberg (pond)	11-2000	0.46
The Netherlands	Marken (lake)	11-2000	0.18
The Netherlands	Ankeveen (river)	11-2000	3.08
		05-2001	1.22
Sweden	Skarsjön (lake)	11-2000	3.49

Source:EUROECOLE (2001)

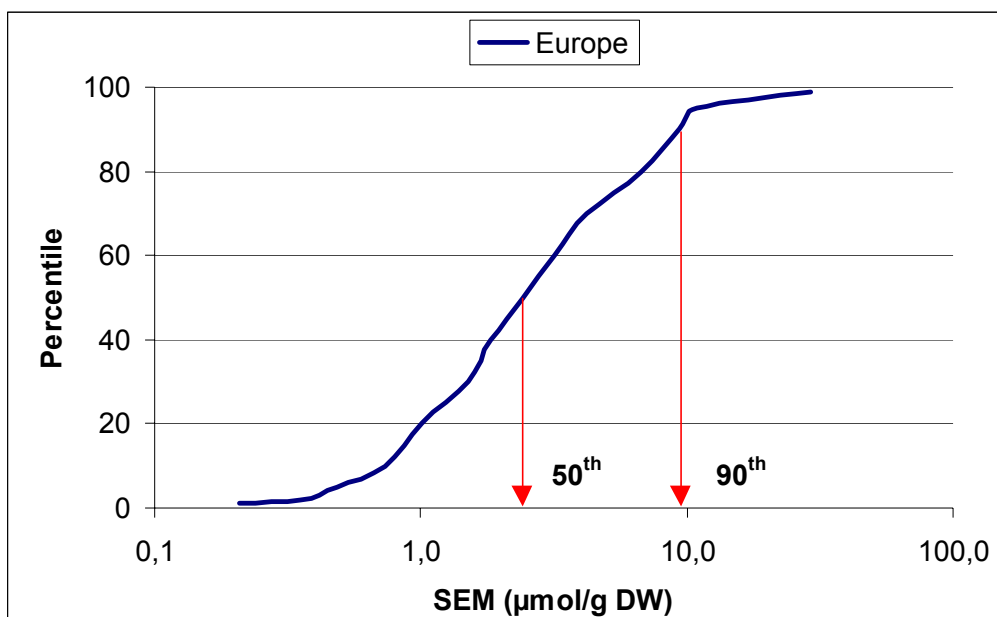
$\Sigma$ SEM concentrations for the different European reference sites varied between 0.35 and 3.5  $\mu\text{mol/gDW}$ . These observations are in concordance with the overall freshwater data set (n = 200) compiled for Flanders where a median SEM concentration of 2.3  $\mu\text{mol/gDW}$ , and a 10<sup>th</sup>/90<sup>th</sup> percentile of 0.8 and 8.5  $\mu\text{mol/gDW}$  respectively could be derived. In figure 7 all data for the other European countries are plotted on the CDF derived from the Flemish data set. From the plot it is clear that the Flemish database provides a good coverage of the other European countries for which  $\Sigma$ SEM data are available.



**Figure 7:** Cumulative Frequency distribution of  $\Sigma$ SEM concentrations in sediments Flanders (Belgium) full line, the Netherlands (red squares) and other European countries (blue squares)

### 3.2.3.3 Overall $\Sigma$ SEM frequency distribution for Europe

All data have been aggregated together in order to elaborate the  $\Sigma$ SEM frequency distribution representative for the whole of Europe (Figure 8). Based on the overall freshwater data set available for Europe ( $n = 226$ ) a median  $\Sigma$ SEM concentration of  $2.4 \mu\text{mol/gDW}$  and a 90<sup>th</sup> percentile of  $9.4 \mu\text{mol/gDW}$  can be calculated.

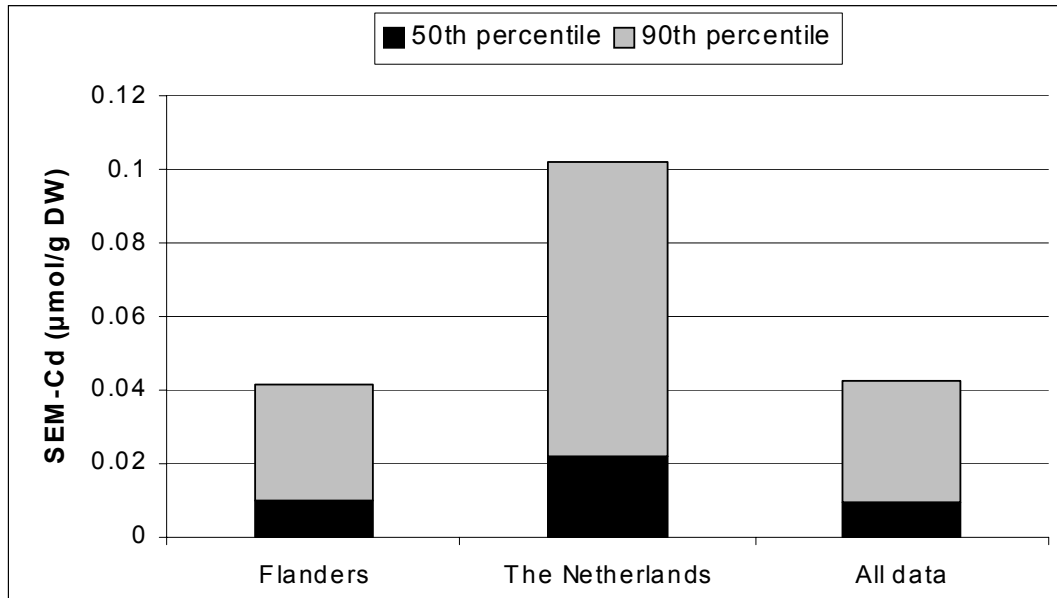


**Figure 8:** Cumulative Frequency distribution of  $\Sigma$ SEM concentrations in European freshwater sediments

### 3.2.3.4 SEM<sub>Cd</sub> frequency distribution for Europe

In applying the SEM-AVS model as outlined above in the risk assessment of a specific metal, such as cadmium, it has to be taken in consideration that  $\Sigma$ SEM represents the sum of several different metals acting in a competitive manner when binding to AVS. To gain a perspective on the concentrations of cadmium measured in sediment samples analysed for SEM, the fraction of the total metal measured is expressed as SEM<sub>Cd</sub>. The median fraction of SEM<sub>Cd</sub> is 0.3 % (i.e., SEM<sub>Cd</sub>/SEM<sub>total</sub> = 0.3 %) for the Flemish database and 0.5 % for the Dutch database. The min-max values for the complete aggregated freshwater database range from 0.01-7 %.

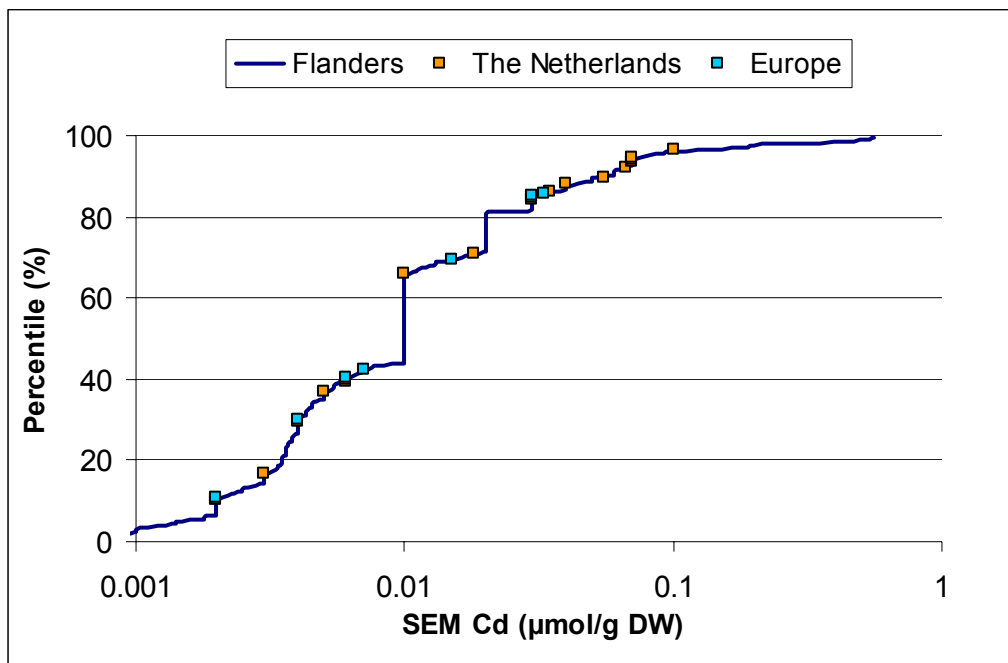
The median and 90<sup>th</sup> percentiles for SEM<sub>Cd</sub> ( $\mu\text{mol/gDW}$ ) for Flanders, the Netherlands and Europe are presented in Figure 9.



**Figure 9:** Ambient SEM<sub>Cd</sub> concentrations ((50<sup>th</sup> and 90<sup>th</sup> percentiles expressed as  $\mu\text{mol/gDW}$ ) in sediments of Flanders (Belgium), the Netherlands and Europe.

Based on the overall freshwater data set ( $n = 226$ ) available for Europe a median SEM<sub>Cd</sub> concentration of  $0.01 \mu\text{mol/gDW}$  ( $1.1 \text{ mg/kgDW}$ ) and a 90<sup>th</sup> percentile of  $0.052 \mu\text{mol/gDW}$  ( $5.8 \text{ mg/kgDW}$ ) can be calculated. The median and 90<sup>th</sup> percentile values of the separate freshwater databases are respectively  $0.01$  ( $1.1 \text{ mg/kgDW}$ ) and  $0.041 \mu\text{mol/gDW}$  ( $4.6 \text{ mg/kg}_{\text{dw}}$ ) for Flanders ( $n = 200$ ), and  $0.022$  ( $2.4 \text{ mg/kgDW}$ ) and  $0.1 \mu\text{mol/gDW}$  ( $11.2 \text{ mg/kgDW}$ ) for the Netherlands ( $n = 16$ ).

Again it should be noted that the observed difference between the Flemish and Dutch data set are mainly due to the choice of distribution function selected to best fit the observed monitoring data. Due to the restricted size of the Dutch database ( $n = 16$ ) a parametric function (lognormal) has been selected to represent best the data points. While the lower data points follow this distribution quite well the upper tail of the distribution deviates more from the really measured data. The latter ranged actually between  $0.003$  and  $0.1 \mu\text{mol/gDW}$  ( $0.3$ - $11.2 \text{ mg/kgDW}$ ).

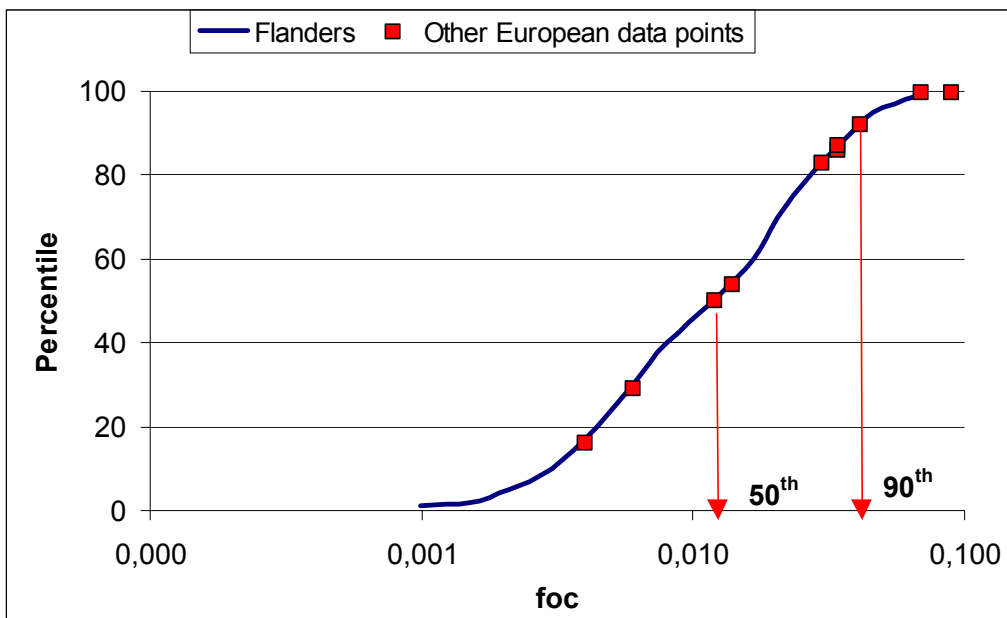


**Figure 10:** Cumulative frequency distribution of  $SEM_{Cd}$  in Flemish and European sediments: Flanders (full line), the Netherlands (red squares) and other European countries (blue squares)

Some of the  $SEM_{Cd}$  data points for the Netherlands are found above the 90<sup>th</sup> percentile of the Flemish data. This is not surprisingly since the Dutch sediments included in the database were in the original studies investigated because they represent contaminated areas (e.g. Ketelmeer and Maar river). The sampling points in the Flanders monitoring network on the other hand have been chosen to represent a mix of reference points, hot spots and moderately contaminated sediments (personal communication Ward De Cooman, VMM, 2003) and as such are more eligible to be used for regional scenario than to base a regional scenario only on some selected rivers with known elevated cadmium concentrations.

### 3.2.4 Organic carbon concentrations in European sediments

The fraction of organic carbon (fOC expressed as gOC/gDW.) in sediments were measured in parallel with the SEM/AVS measurements for the Flemish and EUROECOLE database. For the Dutch database fOC was most often not reported. In figure 11 all available data for the other European countries are plotted on the CDF derived for the Flemish data set.



**Figure 11:** Cumulative Frequency distribution of foc concentrations in sediments of Flanders (Belgium), the Netherlands and other European countries

Based on the overall freshwater data set ( $n = 200$ ) available for Flanders (Belgium) a median fOC concentration of 0.012 (= 1.2 % O.C) and a 90<sup>th</sup> percentile of 0.038 (= 3.8 % OC) can be calculated. The organic carbon concentrations in the other European countries range between 0.006 (= 0.6 % OC) and 0.09 (= 9 % OC) and are well within the range of the Flemish CDF. The observed 90<sup>th</sup> percentile is still below the proposed TGD default value of (0.05g OC/g<sub>dw</sub> or 5 % OC).

The report provides the comprehensive risk assessment of the substance cadmium metal and cadmium oxide. It has been prepared by Belgium in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to humans and the environment, laid down in Commission Regulation (EC) No. 1488/94.

## Part I - Environment

This part of the evaluation considers the emissions and the resulting exposure to the environment in the production of cadmium metal and cadmium oxide, the use of these substances in the production of stabilisers, pigments, alloys and plated products. Further downstream uses are not or only limitedly included. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic and terrestrial compartment has been determined. No risk assessment was performed for the atmosphere or the marine environment. Based on newly generated ecotoxicity data under low water hardness conditions (See Addendum), no risk was identified in the soft water ranges tested. The risk remains uncertain in extremely soft waters (i.e. below 5 mg CaCO<sub>3</sub>/L).

The environmental risk assessment concludes that there is concern for the aquatic ecosystem at certain metal production, processing and NiCd batteries recycling sites. A concern for the sediment compartment is identified for the cadmium plating and alloys sector. Taken into consideration Cd bioavailability in sediments, additional risk is found at specific cadmium metal production, cadmium pigment production and cadmium recycler sites, and under specific disposal scenarios (See Addendum). For the terrestrial compartment a risk is identified at cadmium plating and alloy production sites. A borderline risk is found for soil cadmium concentrations leading to secondary poisoning. Furthermore, there is concern for microorganisms of the wastewater treatment plants of certain NiCd battery recycling plants.

## Part II - Human Health

This part of the evaluation is published in a separate document.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commission's committee on risk reduction strategies set up in support of Council Regulation (EEC) N. 793/93.