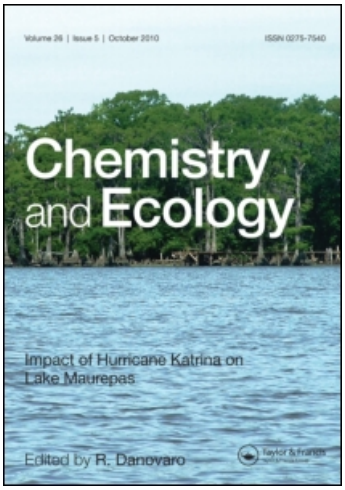

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Distribution of heavy metals in dissolved, particulate and biota in the Scheldt estuary, Belgium

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Distribution of heavy metals in dissolved, particulate and biota in the Scheldt estuary, Belgium

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The distribution of heavy metals in abiotic phases (dissolved, particulate) and biotic fauna (i.e. *Mytilus edulis*), were analysed and studied in the Scheldt estuary, with the aim of determining the distribution of heavy metal pollution, at seven sites. For the analysed metals, the concentrations in *M. edulis* tissues were in the order: Fe > Zn > Cu > Pb > Cd > Co. Cadmium concentrations were the lowest for all sites, except at Borsele and Hansweert. The metals in mussel tissues correlated well with metals in both the particulate (e.g. Cd, $r = 0.98$) and dissolved phases (e.g. Cd, $r = 0.57$; Cr, Zn, $r = 0.79$; Fe, $r = 0.58$). Furthermore, a relationship between heavy metal concentrations in the abiotic phases and the soft tissue of *M. edulis* was developed, with an effort to determine how much pollution apportionment each abiotic phase contributed to metal accumulation in the soft tissues. Results showed that the contribution from the dissolved phase was more significant compared to the particulate phase. The bioaccumulated heavy metals (e.g. Cd, Cu, Zn) in the tissues were way above the acceptable limits stipulated by international codes of practice, implying critical estuary pollution in the biota.

Keywords: metal distribution; heavy metals; dissolved phase; particulate phase; biota

1. Introduction

In recent years, technological advancement in various fields has led to increasing input of heavy metals into the environment, which in turn has inevitably caused marine environmental pollution. Anthropogenic activities have gradually caused metals to be released from their stable forms into the environment [1,2], leading to the overburdening of the natural biogeochemical cycle.

When heavy metals enter into marine environments, they are usually partitioned into; dissolved, suspended particulate matter (SPM), biota and sediment phases. Metals within each phase tend to be distributed into different species [3–5]. These phases into which the heavy metals get assimilated, coupled with interactions within the same phases, tend to determine the final destination of metals in the environment [6–8]. It also determines the availability of metals for uptake by the organisms which live in that particular environment [9–11].

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The partitioning coefficient (K_d) depends on the degree of distribution of metals into various chemical forms for the abiotic environment in question, and the environmental parameters in operation [3,12]. Suspended particulate matter for example, due to their high organic matter content, carrier nature of their oxides, and size (high surface area); scavenge heavy metal pollutants while settling throughout the water column, in this regard, sediments are often rich in contaminants [12–15].

Since marine organisms sometimes tend to switch their habitation in abiotic environments, they are usually exposed to metallic pollutants in those habitats [5,9–11]. *M. edulis* for example, being efficient filter feeders, are capable of taking and concentrating particles from the water column into their bodies [4,9,10]. This is therefore a potential contaminant pathway into their organs [5,16].

There is need to continuously assess the effects of metal exposure, plus the extent of pollution in ecosystems [9,17–19]; while considering all the exposure pathways [3,5–7,16,20–22]. The heavy metals which are adsorbed by particles usually become available to the organisms after ingestion and are then digested into their organs [4,5,9,10].

Although there are many studies on mussels (*M. edulis*), quantitative extrapolation of environmental exposures from metal body concentrations or vice versa, there are still many irregularities and uncertainties [8,23]. Therefore, a clear understanding of the influencing factors is crucial, so as to establish relationships that relate tissue metal concentrations to external exposure.

For example, Phillips [24] recognized the potential effects of environmental variables on the accumulation of metals in mussels. Since then, the influence of many factors have been studied, such as salinity, temperature, season and organic matter [17,25,26], body size [27–30], sex and reproductive status [31,32], habitat fluid chemistry [33], age [31], tidal height [24,27,34] and physiological conditions [31,32].

The main aim of this study is to determine the distribution of heavy metal pollution in the dissolved and particulate phases, plus biota (i.e. *M. edulis*), at seven sites of the Scheldt estuary. Also, since *M. edulis* has proved to be a reliable pollution bio-indicator in the marine environment [5–8], it is hoped that the data of this study will help in beefing up future evaluations of potential hazards to human health for the estuary. Furthermore, a relationship between heavy metal concentrations in abiotic environments and the soft tissue of *M. edulis* is developed, with an effort to determine how much pollution apportionment from the dissolved and particulate phases contribute to heavy metal accumulation in the soft tissues of *M. edulis* bivalves.

2. Materials and methods

2.1. *The Scheldt estuary*

The River Scheldt (Figure 1) starts from the Northern part of France (St Quentin) and empties into the North Sea near Vlissingen (The Netherlands). It has a total length of 355 km and its mean depth is about 10 m [35,36]. Together with all its tributaries, the River Scheldt is also fed by the surrounding catchment area, which causes the discharge to vary considerably; with maximum discharges ($400\,m^3\,s^{-1}$) occurring in winter and spring, and minimum discharges ($20\,m^3 s^{-1}$) during summer and autumn [36].

The river is used as a major drain for industrial and domestic wastes. Some of these wastes are not well treated prior to discharge. For example, in the upper estuary from the industrial area around Antwerp, pollutants are directly drained into the river. This has led to poor water quality in the larger part of the river and the eastern part of the estuary [36]. The dissolved metal concentrations in the Scheldt estuary are higher than the background levels in seas and oceans, which indicate that the estuary is polluted [35].

The concentrations of dissolved Cadmium (Cd), Copper (Cu), Lead (Pb), and Zinc (Zn) for example, are respectively about 20, 20, 4 and 9 times higher compared to the least polluted estuaries elsewhere, e.g. Lena (Russia) [36]. Metal concentrations in the particulate phase are also higher in the Scheldt estuary compared to the Lena estuary in Russia [36,37]. Comparatively, in terms of water discharge, the River Lena gushes 525 km^3/yr, ranking seventh in the world, draining into the Arctic Ocean [37]. It has several tributaries and forms a vast delta covering a total catchment area of 32,000 km^2; with an underlying geology of mainly sandy sedimentary rocks of refractory terrigenous constituents [38].

2.2. *Sampling campaigns*

The locations of the sampling sites are as depicted in Figure 1. In total, seven sampling sites in the Scheldt estuary were selected and sampled (Five from the western part and two from the eastern part). Samples were collected from the estuary along the decreasing salinity gradient from Domburg, Westkapelle, Vlissingen, Borsele and Hansweert (stations coded with numbers; 1, 2, 3, 4 and 5 respectively). The above sites are located in the Western part of the Scheldt estuary. Samples were also collected from the eastern part at Wemeldinge and Yerseke (coded with numbers 6 and 7). All samples were collected in winter (from 30 January 2002 to 13 February 2002), i.e.during low tide periods.

All materials in contact with the samples during sampling campaigns, all glass and plastic ware (sampling bottles, low density polyethylene (LDPE), high density polyethylene (HDPE) bottles, funnels, crucibles, petri dishes, etc) were subjected to the decontamination process; by filling and storing them in 5 to 10% nitric acid (HNO_3, Pro analysis) at room temperature for at least 24 h prior to use, rinsing at least three times with Milli-Q-water. Thereafter, they were then dried in a lamina flow hood. The collected samples were; water, sediment and mussel samples.

Figure 1. A map showing the Scheldt estuary and location of the seven sampling sites.

2.3. *Water samples*

Water samples were collected by hand during low tide, using acid washed (5% HNO_3) high density polypropylene (HDPPE) containers (20–50 litres), at a depth not exceeding 1.5 metres. Before filling, the containers were rinsed at least three times with field water. After collection, samples were immediately transported to the laboratory within 8 h for further analysis.

Physico-chemical parameters such as pH, temperature and salinity were also measured in-situ using a pH meter (pH meter, Hanna Instruments, USA), mercury thermometer (Ters Electronics Ltd., China) and salinometer (YSI, USA; Model 33), respectively. In the laboratory, 600–800 ml of water samples were filtered through 0.2 μm filter membranes (Fairway I. and E. Co. Ltd., China) using a dead end filtration system (T. J. Exp. Equipment Co. Ltd., China), which was connected to purified nitrogen gas that generated filtration pressures, in order to separate the dissolved phase from particulate phase [39].

The filters were then rinsed with 30 ml of Milli-Q-water, so as to remove sea salt. They were then placed on petri dishes, stored in a freezer at −20 °C, till further analysis. The dissolved phase was acidified with 1 ml of 70% nitric acid (HNO_3, ultra-pure) to a pH of 2, and then stored in a refrigerator at 4 °C. Pre-concentration procedures were carried out to extract the dissolved metals [35,39].

The extracted dissolved metals were stored in refrigerators, until measurements using atomic mass spectroscopy (ICP–MS) (Agilent Tech. Co. Ltd., USA) were conducted. During filtration, blank samples were prepared along with the samples, by filtering an equal volume of Milli-Q-water using filter papers and they received similar treatment procedures as the samples.

Dissolved trace metals were extracted from the sea water samples using the freon–dithiocarbamate extraction-back method [35,36]. Suspended particulate matter was extracted following Van Ryssen et al. [40,41], mimicking their total acid digestion procedures. The quality of the extraction method (For dissolved phase) was controlled by analysing blank and reference water samples [BCR-CRM 403] supplied by the Commission of the European Communities; while for suspended matter, blank samples and reference sediment samples [BCR-CRM 320] supplied by the Commission of the European Communities, were analysed alongside the samples.

2.4. *Mussels*

About thirty-five (35) mussels were collected from each site during low water tide periods (depth up to 1.5 metres), close to the low water shoreline, at a distance not exceeding 30 metres from the shoreline. The samples were put in plastic bags, immediately stored in iceboxes and then transported to the laboratory. At the laboratory, samples were cleaned and washed, in order to remove epibionts (algae, barnacles or any deposits in the animal shells).

Care was taken during cleaning to avoid any material or water that could otherwise contaminate the samples. After cleaning, mussels were then incubated in dishes using field water samples, for at least 24 h for depuration. The animals' shell lengths were then measured using an electronic digital caliper (Tide M. T. S. Co. Ltd., China). The mussels were finally dissected using a stainless steel scalpel blade, to extract their soft tissues.

The tissues were then placed in pre-weighed clean 50 ml polypropylene vessels and their wet weights were recorded prior to drying in the oven at 60 °C, for at least 72 h. Soft tissues were dried to constant weight, wrapped in parafilm; in order to prevent sticking. The drying methods employed here have been successfully used in other studies [42,43]. Lastly, the dry weights were measured using an electronic balance and the tissues were then digested using a microwave oven. The method was checked by analyzing mussel tissue reference material [VMK 102] supplied by the Commission of the European Communities.

The techniques which were used are based on principles of inductively coupled plasma atomic mass spectroscopy (ICP–MS) (Agilent Technology Co. Ltd., USA) and inductively coupled plasma atomic emission spectroscopy (ICP–AES) (Agilent Technology Co. Ltd., USA), which are used to determine a large variety of chemical elements in a short time. The working specifications and parameters were followed as specified by the instrument manufacturers and as stipulated by APHA et al. [39]

Correlation and non-linear regression methods were partly used for data analysis. The correlation and regression coefficients (r and r^2), and the significance levels (p) were also employed to evaluate the significance of the estimated parameters. All statistical analyses, particularly analysis of variance (ANOVA) were performed by using SPSS version 12.0 for Microsoft Windows (dated September 2003, SPSS Inc., 1989–2003) to determine significant differences in the results between the study sites, for both abiotic phases and biota.

3. Results

3.1. *Analytical quality assurance*

The accuracy of the digestion method was checked by analysing mussel standard reference material [VMK 102] supplied by the Commission of the European Communities and river sediment standard reference material [BCR-CRM 320] supplied by the Commission of the European Communities with known elemental concentrations. A good agreement was obtained between the experimental and the certified values of both VMK 102 and CRM 320, as depicted in Table 1.

3.2. *Dissolved metal concentration*

The Mean concentrations ($n = 3$) of heavy metals in the dissolved phase for the seven sampling stations are presented in Figure 3. All metals in the dissolved phase were relatively higher for sites 3, 4 and 5. The highest dissolved levels of each metal were found in samples from the Western part of the Scheldt estuary, with metal concentrations decreasing down the estuary, along the increasing salinity gradient. ANOVA test resulted into significant difference in metal concentrations among the sampling site (Table 2). Multiple comparison (*posthoc* analysis) test confirmed the significant differences among the studied sites for all ANOVA tests which was significant at $p < 0.05$ (Table 2).

Furthermore, Zn concentration was highest for all sites, followed by Fe and Cu. Other metals were present at appreciable concentrations except Cd (stations 1 and 7) and Pb (station 1, 6 and 7)

Table 1. Mean experimental and certified values with their standard deviations in parentheses. VMK 102 mussel reference material ($n = 5$) was used for mussel tissue quality assurance while CRM 320 river sediment reference standard material ($n = 6$) was used for both river sediment and suspended particulate matter. nd. = not done.

	Metals in mussel tissue (mg/g)		Metals in (SPM) (μg/g)	
Metal	Experimental	Certified	Experimental	Certified
Cd	3.90 (0.30)	2.90 (0.20)	0.50 (0.02)	0.53 (0.03)
Cu	10.48 (0.60)	10.30 (0.70)	39.01 (1.61)	44.10 (1.00)
Fe	182.70 (5.60)	192.00 (5.00)	nd	nd
Zn	124.00 (2.10)	114.00 (1.40)	139.37 (2.69)	142.00 (3.00)
Co	nd	nd	17.48 (0.57)	19.00 (0.69)
Pb	nd	nd	38.36 (4.58)	42.30 (1.60)

Table 2. ANOVA[†] table showing differences in metal concentration among the biotic and abiotic phases at different studied sites.

	Metal	Sum of Squares	df	Mean Square	F	*p*-value
Tissue	Pb	76481.46	6	12746.91	1625.79	0.000
	Cd	46.50	6	7.75	4737.73	0.000
	Co	5126.45	6	854.41	1564.81	0.000
	Zn	1796362.50	6	299393.76	17.29	0.000
	Cu	22015.03	6	3669.17	1367.33	0.000
	Fe	158000.54	6	262751.98	1285.49	0.000
Dissolved	Pb	64870.42	6	9876.82	1485.25	0.000
	Cd	44.88	6	6.18	3825.82	0.000
	Co	4856.64	6	685.84	1446.18	0.000
	Zn	1412274.20	6	17313.99	14.92	0.000
	Cu	20213.27	6	2863.68	1133.36	0.000
	Fe	134562.08	6	204398.74	1056.92	0.000
Particulate	Pb	44686.17	6	8627.72	1050.63	0.000
	Cd	38.18	6	5.72	3948.24	0.000
	Co	4514.06	6	608.34	1124.82	0.000
	Zn	1028168.05	6	12184.26	12.88	0.000
	Cu	17846.22	6	2286.34	898.26	0.000
	Fe	99868.84	6	189698.52	994.84	0.000

[†]Multiple comparison (*Post hoc*) analysis was conducted for all ANOVA results which were significant at $p < 0.05$, which depicted significant different in metal concentration among sampling sites except at Yerseke and Borsele (sampling sites 6 and 7).

where the concentrations were low. There was significant correlation ($p < 0.05$) between metal concentrations in the dissolved phase and those in the particulate phase, for all sites. Significant correlations ($p < 0.05$) were also shown for metals in both the dissolved phase with those in the tissues of *M. edulis*.

3.3. *Metal concentration in suspended particulate matter (SPM)*

The concentrations of each metal for all sampling stations are as presented in Figure 4. The concentrations of Zn were highest of all metals for all sites, followed by Fe and Pb. There were significant correlations ($p < 0.005$) between metals in the particulate phase with metals accumulated in the tissues of *M. edulis* (Figures 2 and 4). ANOVA test resulted into significant difference in metal concentrations among the sampling site (Table 2).

In order to determine how much pollution apportionment each abiotic phase contributed to metal accumulation in the soft tissues, further analysis was carried with the aid of a 'two-phase uptake model', shown in Table 3 results (non-linear estimation mathematical equation), for all correlations which were significant ($p < 0.05$). A summary of the results of this model are as depicted in Table 3. The analysis was performed to assess the contribution of metals accumulated in the tissues, both for low and high metal concentrations in the dissolved phase.

At both low and high metal concentrations in the dissolved phase, the contribution from the dissolved phase was significantly higher ($p < 0.05$) than that of the particulate phase for all metals except Cu, Cd; whose converse was true and significant as well ($p < 0.01$).

Moreover, the contribution from the dissolved phase towards metals accumulated in the *M. edulis* tissues was more significant (e.g. $r = 0.79$, $p < 0.05$) than that of the particulate phase, for both low and high metal concentrations in the particulate phase. The percentage contributions from particulate and dissolved phases during both low and high metal concentration in either particulate or dissolved phase were as clearly depicted in Table 3.

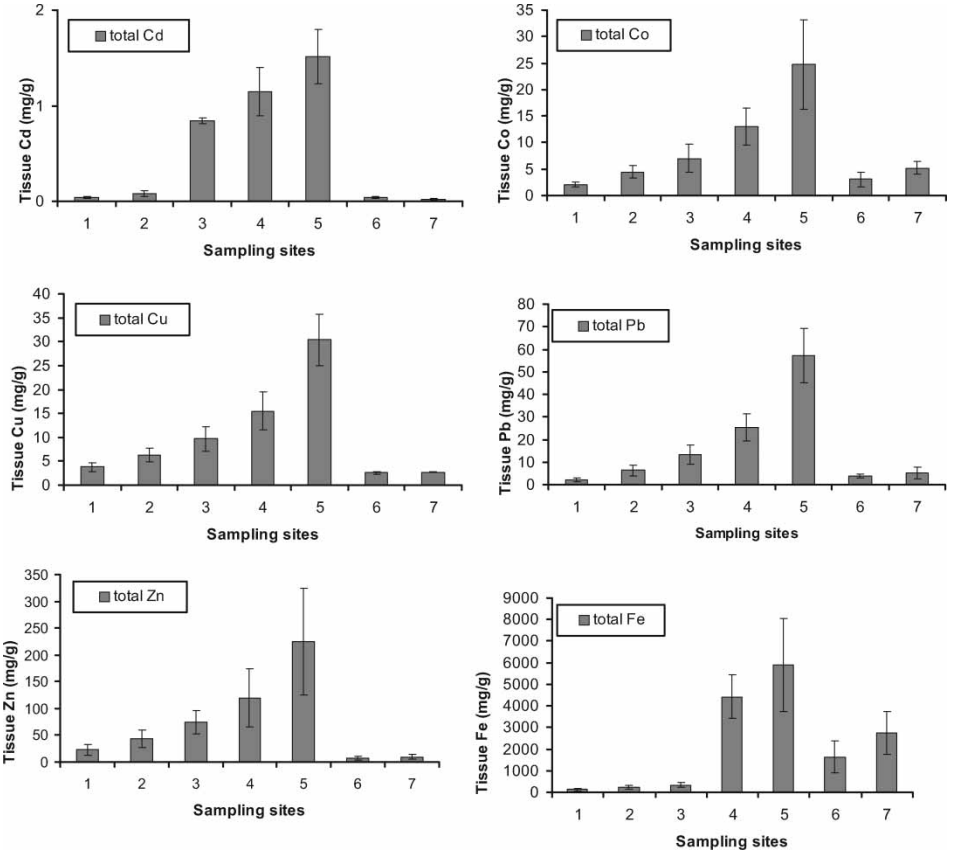

Figure 2. Heavy metal concentrations in *M. edulis* tissues (mg/g) for the seven study sites. The bars represent mean concentration values and the whiskers are the standard deviations of the means.

Table 3. Correlation coefficient (r^2) showing relative significance of accumulation from both particulate and dissolved phases into mussel tissues for low and high metal concentration: The output of the model $V_{MT} = a + b \times V_{part} + V \times C_{diss}$.

Abiotic phase	Metal	r^2 (low metal in dissolved phase) %	p-value	r^2 (high metal in dissolved phase) %	p-value
Particulate phase	Pb	0.15	0.050	0.54	0.000
	Cd	0.46	0.000	0.96	0.000
	Co	0.35	0.015	0.56	0.000
	Zn	0.39	0.012	0.57	0.000
	Cu	0.19	0.048	0.23	0.043
	Fe	0.22	0.045	0.30	0.019
		r^2 (low metal in particulate phase) %		r^2 (high metal in particulate phase) %	
Dissolved phase	Pb	0.21	0.043	0.47	0.000
	Cd	0.33	0.017	0.55	0.000
	Co	0.49	0.000	0.75	0.000
	Zn	0.36	0.015	0.63	0.000
	Cu	0.24	0.042	0.45	0.000
	Fe	0.26	0.040	0.38	0.013

3.4. *Metal concentrations in the tissues of M. edulis*

Figure 2 depicts the mean concentrations ($n = 35$) of heavy metals in the tissues of *M. edulis*, from the study sites in the Scheldt estuary. The graphs depict almost similar trends of bioaccumulation for all metals for all the sites. The order of magnitude of bioaccumulation of metals showed more or less similar patterns, i.e. Fe > Zn > Cu > Pb > Cd > Co. Comparatively, Cd levels were quantitatively low at all sites, except for sites 3, 4 and 5.

Correlation analysis was performed to check for significance between heavy metals accumulated in the tissue, plus both dissolved and particulate metals. All metals except Co and Cu depicted accumulation in soft tissues. Co showed significant accumulation for only particulate phase, but not in the dissolve phase; while Cu depicted significance only in the dissolved phase. ANOVA test depicted significant difference in tissue metal loads among the sampling site, with lowest tissue metal concentration at the mouth of the estuary (Table 2).

4. Discussion

4.1. *Heavy metal in M. edulis tissues*

The concentration of heavy metals in the tissues of *M. edulis* was significant and it showed bioaccumulation effect from the abiotic phases. For most metals, there were higher metal concentrations in *M. edulis* tissues than from the abiotic phases. Marine mussels such as *M. edulis* can substantially accumulate heavy metals into their tissues at higher concentrations relative to their ambient environments [4,9,10], due to their filtration-feeding mode abilities and two-way exposure pathways [5,16].

Although the heavy metal concentrations in the dissolved phase were generally within the permissible limits, also the results (ref. Figures 2, 3 and 4) clearly show that that the concentrations of some heavy metals, such as Cd, Cu, and Zn, in both the particulate phase and *M. edulis* soft tissues exceed the maximum permissible levels of 2 μg/g for Cd, 10 μg/g for Cu, and 100 μg/g for Zn, respectively; as stipulated in the international standards of WHO [44].

In addition to the above, the results of metal concentrations in *M. edulis* tissues for this study are way above those that were reported in water ecosystems elsewhere [42,45]. Wang et al. [46] reported that mussels can selectively accumulate certain elements. This selectivity is the most important criterion in choosing species as bio-monitors. That 'selectivity trait' is what makes mussels like *M. edulis* work very well as potential bio-monitors for certain metals, to monitor heavy metal pollution. However, in this study, this trait on metal bioaccumulation was not observed.

Heavy metal (Cd, Co, Cu, Fe and Zn) concentrations in mussel tissues were higher at Domburg and Hansweert compared to the background levels given by Riget et al. [28]. Cadmium in Mussels from Hansweert was 14 times higher than that reported earlier by Riget et al. [28]. Mussels are primarily exposed to both particulate and dissolved phases and secondarily to sediment, as food uptake pathways. These pathways are without question potential sources of toxic metals to *M. edulis*.

This study demonstrated that metals in both dissolved and particulate phases do contribute significantly to metals accumulated in *M. edulis* tissue. There were correlations between metals in the dissolved and particulate phases to those in the tissue of mussels, implying that these are crucial pathways for metal uptake and consequent bioaccumulation (Table 3 and Figure 5). Luoma et al. [21], Wang et al. [47], and Wang and Fisher [22] reported that the particulate phase was an important pathway, as far as uptake of metals by marine bivalves was concerned.

In this study, the output of the non-linear estimation model results in Table 2 show that the dissolved phase is indeed an important metal uptake pathway into *M. edulis* organs, compared to

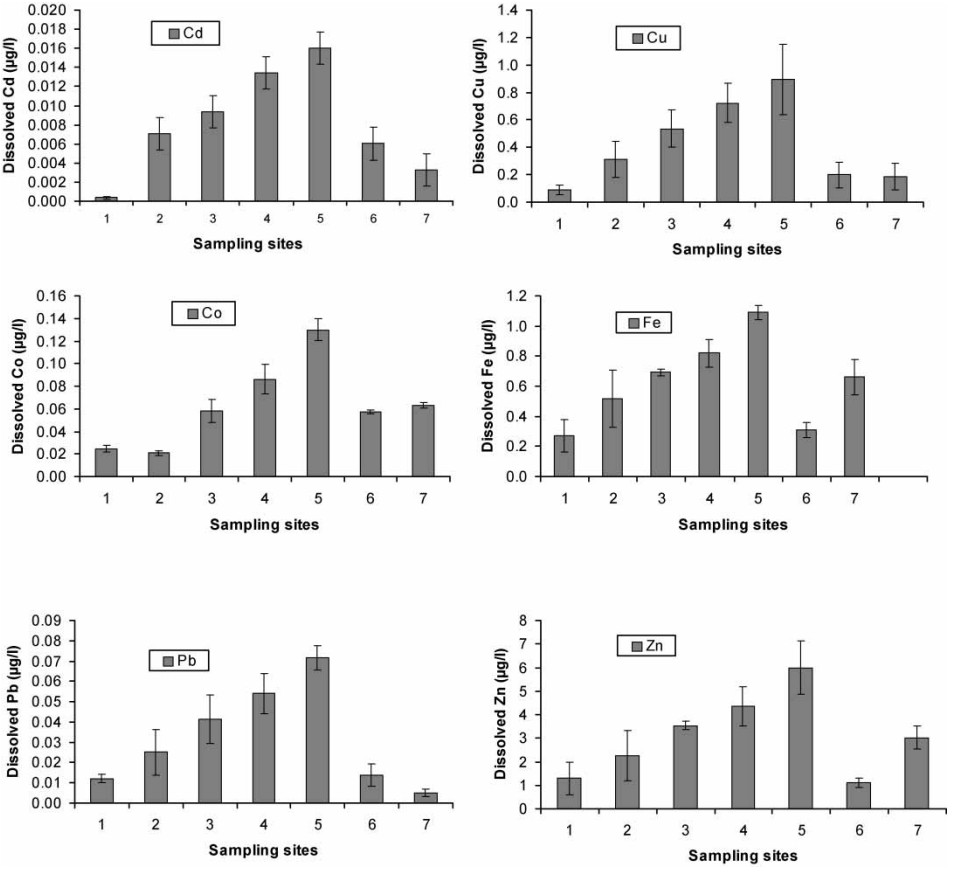

Figure 3. Dissolved heavy metal concentrations (µg/l) for water samples taken from the seven study sites. The bars represent mean concentration values and the whiskers are standard deviations of the means.

the particulate phase. As mentioned earlier, the non-linear estimation model was handily applied in order to scrutinise the significance of individual contributions between dissolved and particulate phases when the concentration of metals were higher in dissolved and/or particulate phases. Thus, the results emphasised the fact that biota pollution emanated from both phases [4,5,16].

Indeed at sites which depicted relatively higher dissolved heavy metal concentrations as shown in Figure 3, i.e. sites 2, 3, 4 and 5; there were correspondingly higher concentrations in the mussel tissues (Figure 2). An increase in the dissolved abiotic phase, gave a similar increasing trend for the tissue concentrations (ref. Figures 2 and 5). This confirms the findings of Rousse et al. [33], who stated that increase in habitat fluid metal chemistry is an important indicative factor that influences increased metal concentrations in organism tissues.

It is crucial to note here that the variability of metal concentrations in the abiotic phases among the studied sites is mainly probably due to upstream industrial activity wastes that are discharged into the Scheldt tributaries [35,36], saline-fresh water wedge and exchange [25,26], plus the nature and geology of the catchment area that usually acts as a carrier of these pollutants into the tributaries [36,37].

Also, among the factors that affect mussel tissues concentrations as discussed earlier in the introduction (Section 1), shore height is reported to be an important and obvious factor, with high potential of causing high individual variability in the contents of heavy metals within *M. edulis* habitats [23,31,32]. In addition, the influence of tidal exposure has not received the

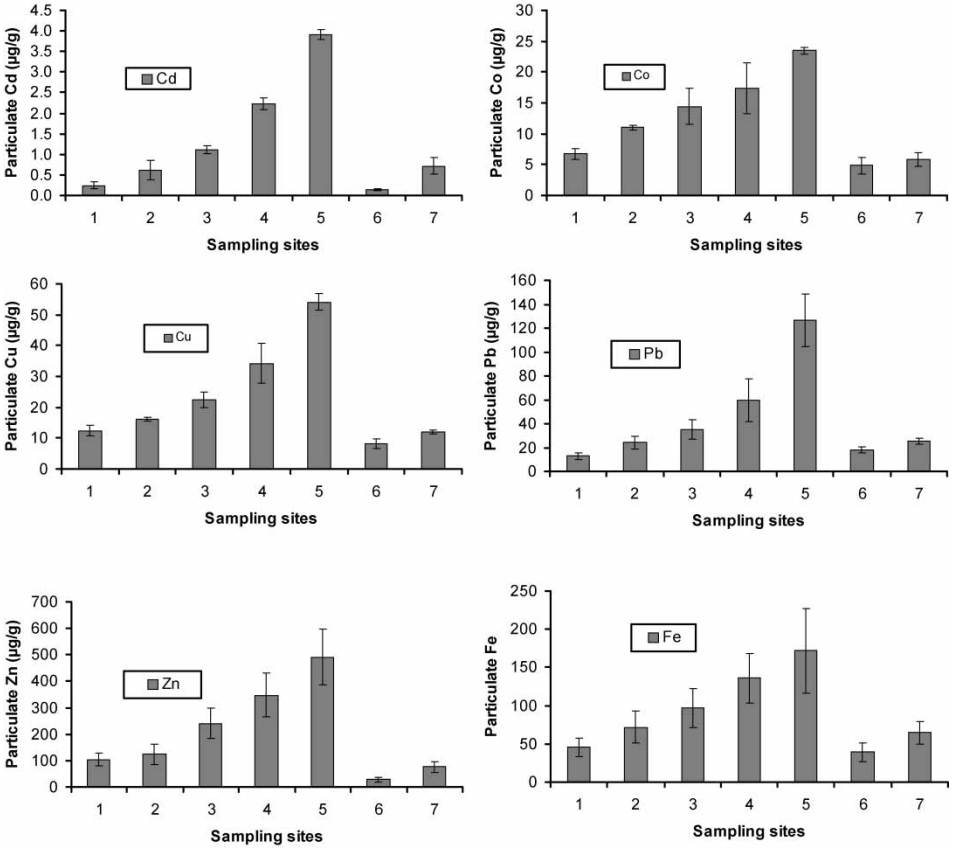

Figure 4. Heavy metal concentrations in the particulate phase, SPM (µg/g) for the seven study sites. The bars represent mean concentration values and the whiskers are standard deviations of the means.

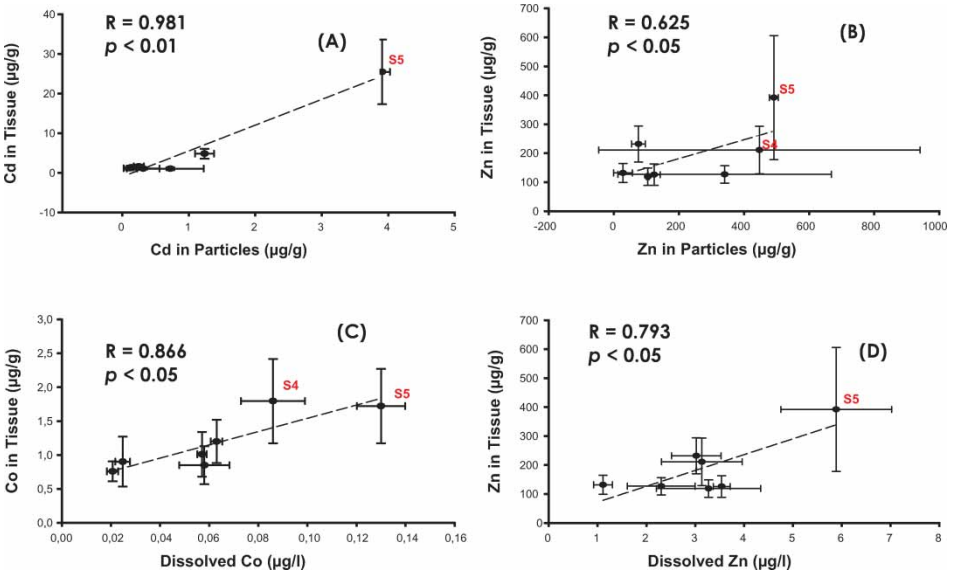

Figure 5. Correlation between metals in the soft tissue of mussels with metals in both dissolved and particulate phases. A and B depict correlations between *M. edulis* tissue metal concentration (mg/g) *versus* particulate phase (µg/g), while C and D depict correlations between tissue concentration (mg/g) *versus* dissolved phase (µg/l).

attention it deserves and in *M. edulis* only few studies involving Cd, Cu, Pb and Zn are on record [24,34]. Neither did this study look at the effects of both shore height and tidal exposure on the bioavailability of metals, since it was carried out during the low tide period.

As shown in Figure 1, the salinity gradient decreases along sites 1 to 5. The same is true for sites 6 and 7. Salinity is another factor that affects heavy metal bioaccumulation in mussels and abiotic phases [17,25,26]. Between sites 1 and 5, during the study period in the estuary, the average decreasing salinity varied between 30.6 and 14.3, respectively. The findings of this study (Figures 2, 3 and 4) showed an increase in heavy metal concentrations in tissues, plus abiotic phases, along the decreasing salinity gradient. Fisher et al. [25] and Vercauteren and Blust [26] reported and discussed similar trends induced by salinity, coupled with temperature. In this study, we didn't analyze temperature effects on heavy metal bio-accumulation.

However, in whole organism experiments, at salinity levels <18 ppt, Phillips [24] detected no temperature effects on accumulation of Cd, Cu, Pb and Zn. Fisher et al. [25] also observed that Cd accumulation by mussels was only significantly decreased at very low temperatures ($<7\,^{\circ}$C). In both studies, temperature exposures were coupled with different salinity treatments, thus it is not categorically clear whether salinity or interaction between the two factors may have influenced the results. Some recent studies have reported uptake that is dependent and increases with increase in temperature, and decreasing salinity [46].

Only Cd showed higher contributions from the particulate phase at both lower and higher concentration of metals. These results are in agreement with the findings reported by Wang et al. [16] except for Cd; which they reported that it could be mainly accumulated by mussels from the dissolved phase. In the model, the uptake from both dissolved and particulate sources were separately measured, and the variability of each parameter was quantified. The model can accommodate metal accumulation under diverse environmental conditions, which the organisms are likely to encounter.

4.2. *Dissolved metal concentration*

The concentration of dissolved metals was highest at site 5. Desorption of metals from both particles and sediment due to the dynamic condition of the marine environment [26], might be the main reason for elevated metals in the dissolved phase, plus the fine grained sediment and the carbon content of the sediment at this site.

Metals which are loosely bound and thus leachable can be mobilised from the particles and sediments into the dissolved phase, thus increasing the concentrations in the water column. However, the metal concentrations of Cd, Cu, and Zn were lower than those reported elsewhere [35,36]. Co concentration was comparable to the results reported by Baeyens et al. [36]. The concentrations of most metals in the dissolved phase depict a decrease compared to the previous few years [35,48].

4.3. *Metal content in the suspended particulate matter (SPM)*

Filtration of seawater in order to obtain enough particles, as reported elsewhere [49–51] was also a challenge in this study. With respect to heavy metal cycling processes, the particulate matter is one of the dominant factors for the transport and exchange of heavy metals between the different phases and water bodies. Most metals such as Pb, Zn and Cu are predominantly bound to suspended matter [50,51].

For most metals in the suspended particles, there was high correlation ($p < 0.05$) to those found in mussel tissues. Due to dynamic conditions of the marine system, metals can be re-suspended from the bottom sediment into the water column, thus exposing them to filter feeding organisms

[14,15]. Also sorption of dissolved metals in water may occur elevating the concentration of metals in the suspended particles [51].

The results of our study revealed considerable metal concentrations in suspended matter of the River Scheldt. It is not the purpose of this study to compare these suspended matter concentrations to previous studies, however, Cd, Cu, and Pb concentrations were comparable to those reported by Baeyens et al. [35]; while that of Zn was higher, and that of As was lower than that reported by Verlaan [52]. Solid phase, particularly when enriched with organics are preferential known metals scavengers, and therefore have the potential of accumulating large amounts of metals.

5. Conclusion

In the above exposé therefore, the following was inferred:

The metals measured in the tissues of *M. edulis* were generally higher than those in the particles and dissolved phase (with few exceptions), showing the effect of accumulation for those metals, with salinity gradient playing a role. Some metals such as Co, Fe and Zn are known to be essential elements to mussel organ development [32], therefore showed relatively low concentrations in tissues.

The relationship between heavy metal concentrations in the abiotic phases and the soft tissue of *M. edulis* was developed, with an effort to determine how much pollution apportionment each abiotic phase contributed to metal accumulation in the soft tissues. Results showed that the contribution from the dissolved phase was more significant compared to the particulate phase. The bioaccumulated heavy metals (e.g. Cd, Cu, Zn) in the tissues were way above the acceptable limits stipulated by international codes of practice, implying critical estuarine pollution in the biota, especially those that can act as bio-indicators like *M. edulis*.

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