

Trace metal speciation at the sediment–water interface of Vidy Bay: influence of contrasting sediment characteristics

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Abstract Trace metal analysis and speciation were performed at the sediment–water interface of Vidy Bay (Lake Geneva, Switzerland). This bay is impacted by hazardous compounds released via the sewage effluent of a major wastewater treatment plant (WWTP). Sediment cores and overlying water were sampled simultaneously at 12 sites characterized by contrasting sediment surface characteristics (color, methanogenic activity, bacterial mat) using corers deployed from a MIR submarine or research boat. The concentrations of trace metals in particulate form in the sediment and dissolved in the interstitial water, as well as the particulate, colloidal and dynamic fractions of trace metals in the overlying water were determined by combining an in situ and laboratory multi-method analytical approach. The results indicate differences in trace metal speciation in the sediment and overlying water at the 12 investigated sites. The observed differences were found to be more correlated to bacterial community, abundance, type and activity than to distance from the WWTP sewage outlet.

Keywords Metal speciation · Sediment · Interstitial water · Overlying water · Bacterial mat · Methanogenesis

Introduction

Vidy Bay, located on the northern shore of Lake Geneva (Fig. 1a), is a sensitive area. It is located <4 km from the pumping station of St. Sulpice that provides <60 % of the drinking water for the inhabitants of the municipality of Lausanne (Fig. 1a). It is the most polluted area of the lake (e.g. Loizeau et al. 2004; Pardos et al. 2004). The main source of pollution is the effluent of the waste-water treatment plant (WWTP) of Lausanne that is released, via a pipe, directly into the bay since 1964. In an attempt to reduce the contamination impact of the WWTP, the sewage effluent pipe outlet, originally located at a depth of 12 m and a distance of 350 m from the shore, was moved in 2004 to a depth of 35 m and to a distance of 700 m from the shore. The study by Poté et al. (2008) showed that the effect of the elongation of the WWTP pipe on contamination of the sediments by hazardous compounds carried by the WWTP sewage effluent, and trace metals in particular was only partially successful.

Metals transported to the sediment can be either buried or remobilized (Van Den Berg et al. 1999) via various diagenetic processes, e.g.: bacterially mediated oxidation of organic matter inducing redox reactions such as oxygen consumption near the water–sediment interface and reduction of nitrate, manganese oxides, iron oxides and sulfate (Froelich et al. 1979). These dynamic redox processes affect metal equilibrium between the solid and liquid phases (via precipitation, adsorption/desorption, sulfide complexation, organic ligand biological degradation, and/or biological uptake processes) and therefore their speciation and rates of transfer across the sediment–water interface. Understanding the role of sediments as either a sink or source of trace metals released by the WWTP sewage effluent in the bay is thus of prime interest for assessment of their long-term impact. For this purpose, investigations based only on the measurements of the total

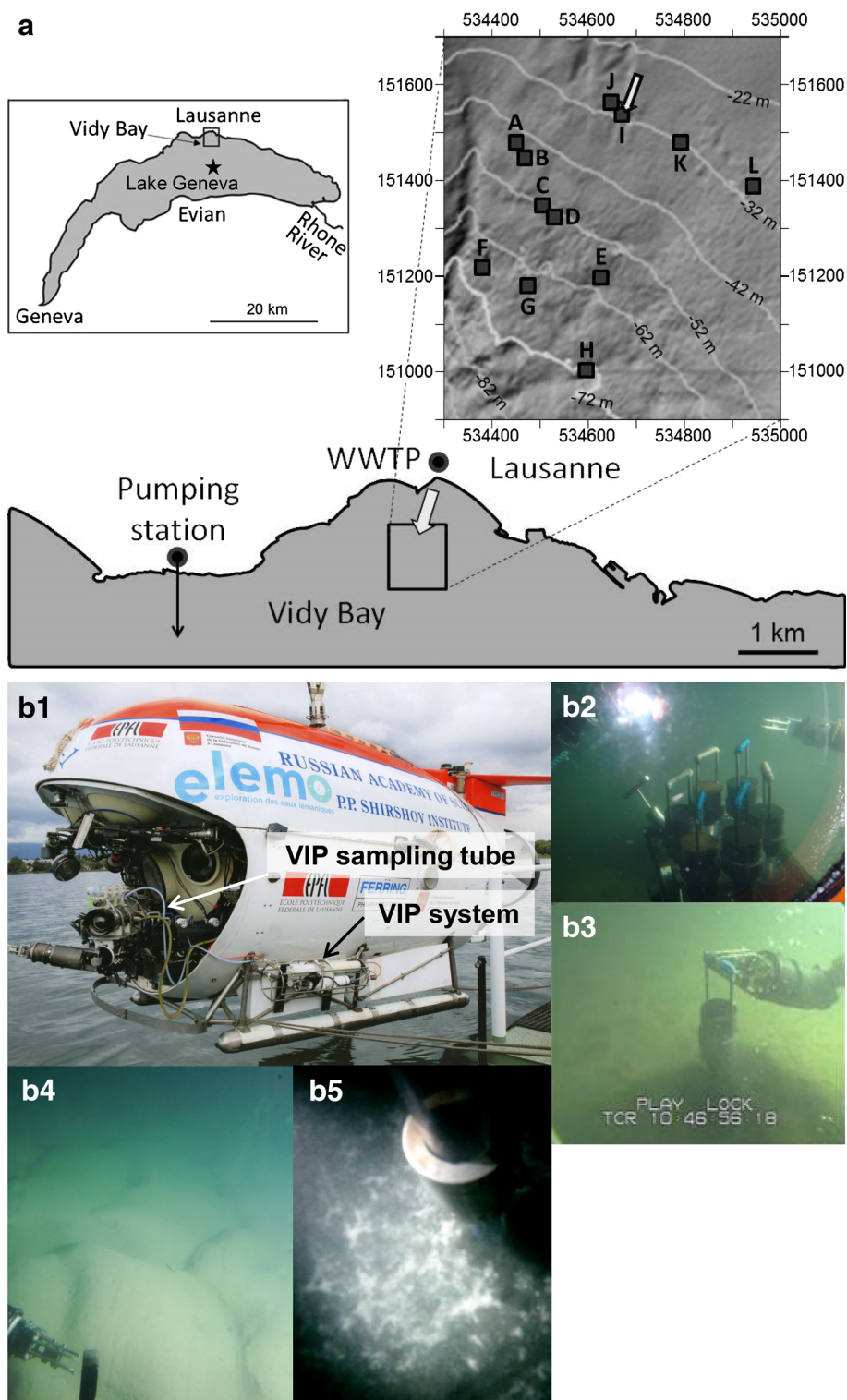
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Fig. 1 **a** Map of the study area, Vidy Bay (Switzerland).

Squares on the map (numbered from A to L) represent the localization of the 12 study sites. The white arrow represents the location of the WWTP pipe end. The black arrow gives the rough location of the pumping station pipe end (1 km from the shore; 50 m depth). The star represents the reference SLH2 station located at the deepest part of the lake, almost halfway between the French and Swiss coastlines.

b Photos of (**b1**) the MIR submarine equipped with the VIP system; **b2** the rosette supporting the corers during the MIR dives; core sampling in sediment characterized by the presence of (**b3**) large white filament-like bacterial mat (e.g. sites D, I, J and K); **b4** high methanogenic activity (e.g. sites A, B, I and J), and **b5** pillow structure (site H)



concentration of metals in the particulate form in the sediment, as performed in all previous studies related to trace metals in the bay (e.g. Arbouille et al. 1989; Monna et al. 1999; Loizeau et al. 2004; Pardos et al. 2004; Poté et al. 2008; Thevenon et al. 2011), are insufficient. Detailed studies of trace metal

speciation at the sediment–water interface as a function of biogeochemical conditions are required.

The aim of this work, as part of the ÉLEMO project (Wüest et al. 2013), was a first step toward such a study. It focused on assessing the influence of sediment characteristics (color,

morphology, methanogenic activity, bacterial mat) on the speciation of trace metals at the sediment–water interface. To achieve this, the “MIR” submarines (Shirshov Institute of Oceanology, USSR Academy of Sciences) and the research boat “La Licorne” (Institute F.-A. Forel, University of Geneva) were used to (1) map the spatial sediment characteristics in a defined geographic area surrounding the WWTP pipe outlet; (2) perform in situ and on-board measurements, respectively, of metal fraction available for bio-uptake; and (3) collect sediment and overlying waters at contrasting sites for complementary analysis of i) particulate and dissolved metal concentrations in the sediment and overlying water; and ii) sediment interstitial and overlying water composition.

Methodology

Field sample collection and measurements

Sampling was performed at 12 sites in Vidy Bay (Fig. 1a): 8 sites (samples A–H) during the MIR dives in July 2011 and 4 sites (samples I–L) during a complementary survey in May 2012 with the research boat “La Licorne” (Institute F.-A. Forel, University of Geneva). These sites, selected from video recordings made during preliminary studies with the MIR submarines and “La Licorne”, were characterized by contrasting sediment surface color, morphology, methanogenic activity and bacterial mat (Table 1; Fig. 1b). At each site, sediment and overlying water were collected simultaneously using Plexiglas corers (5.7 cm in diameter and ~60 cm length). These devices were manipulated by the arm of the MIR submarine during

each dive (Fig. 1b2, b4) or were sunk by gravity when deployed from the boat (Fig. 1b3). The cores were hermetically sealed as soon after their retrieval on board to prevent O₂ penetration and were rapidly transported to the laboratory for specific sampling in a glove box under N₂-atmosphere.

The overlying water was first sampled using washed PP syringes and tygon tubes. An aliquot of raw water was collected and acidified to pH 1 with HNO₃ suprapur for the analysis of the total acid extractable particulate metal (Me_T) concentrations at pH 1. A second aliquot was filtered through 0.45 μm pore size acetate cellulose membranes (Whatman) and acidified with HNO₃ (suprapur 14 M, 1 % v/v) for total dissolved metal (Me_D) analysis. The upper part of the sediment was then sliced into three layers (0–1.5, 1.5–3 and 3–6 cm) with plastic cutters. The outer part of the sediment core in contact with the side of the corer was discarded. Each sediment slice was placed into 50 ml HNO₃ cleaned PP centrifuge tubes (Greiner©) and immediately centrifuged at 3,500 rpm for 40 min to extract pore waters. The pore water samples were filtered in the glove box (under N₂-atmosphere) using 0.45 μm pore size acetate cellulose membranes (Whatman) and acidified with HNO₃ (suprapur 14 M, 1 % v/v) for total dissolved interstitial metal (Me_I) analysis. All samples for measurements of Me_I, Me_T and Me_D were stored at 4 °C in the dark prior to analysis. Sediments were lyophilized using a CHRIST BETA 1–8 K freeze-drying unit (–54 °C, 6 Pa), and then crushed in an agate mortar. Representative subsamples (~30 mg) of lyophilized, powdered and homogenized sediment were digested in 750 mL HCl (12 M suprapur) and 250 mL HNO₃ (14 M suprapur) in closed Teflon

Table 1 Description of the 12 study sites in Vidy Bay

Site	WGS84 coordinates		SWISS coordinates		Distance from outlet pipe (m)	Depth (m)	Sediment observations		
	Latitude (° decimal)	Longitude (° decimal)	X (m)	Y (m)			Bacterium mat	Methane degassing	Color
A	46.511417	6.584550	534,450	151,481	232	42	∅	M+	Light brown–small white spots
B	46.511133	6.584783	534,468	151,449	226	42	B–	M+	Light brown–small white spots
C	46.510233	6.585267	534,504	151,349	258	46	B–	M–	Light brown–black and white spots
D	46.510033	6.585617	534,530	151,326	261	51	B+	M–	Light brown–black spots
E	46.508883	6.586883	534,626	151,197	350	52	∅	∅	Light brown–black and white spots
F	46.509050	6.583667	534,379	151,218	439	61	∅	M–	Light brown
G	46.508717	6.584933	534,476	151,180	414	60	∅	∅	Light brown
H	46.507150	6.586533	534,597	151,005	544	70	∅	∅	Pillow/trench structures
I	46.511989	6.587403	534,670	151,540	5	31	B+	M+	Heterogeneous with wastes
J	46.512212	6.587112	534,648	151,565	33	31	B+	M+	Heterogeneous with wastes
K	46.511462	6.589014	534,793	151,480	136	32	B+	∅	Heterogeneous with wastes
L	46.510649	6.591007	534,945	151,388	314	27	∅	∅	Light brown

For the sediment observations, three qualitative criteria were considered: presence or absence of bacterial mat (B+, large bacterial mat; B–, small bacterial mat; ∅, absence of bacterial mat), methanogenic activities (M+, gas bubbles observed continuously; M–, gas bubbles observed during core sampling; ∅, absence of bubbles) and color of sediment

reactors (Savillex©) on a heating plate (2 h at 110 °C). The Teflon reactors were then opened and heating processes continued until complete evaporation of the reagent solution. The dry residues were re-dissolved in 150 mL HNO₃ (14 M suprapur) at 70 °C for 15 min. After cooling, final sample volumes were brought to 10 mL with ultra-pure water (Milli-Q) and stored at 4 °C in the dark prior to analysis.

A voltammetric in-situ profiling (VIP) system, incorporating a GIME sensor (Tercier-Waeber and Taillefert 2008), was used at each site to perform direct square-wave anodic stripping voltammetric (SWASV) measurements of the concentration of the dynamic fraction of Cd, Pb and Cu (Me_{dyn}) in the overlying water. This fraction, defined as the sum of the concentration of the free metal ion and labile metal complexes with size typically of few nanometers, is relevant in terms of ecotoxicity assessment as it represents the maximum fraction of metal potentially bioavailable (Buffle and Tercier-Waeber 2005). Reliable measurements of this metal fraction using traditional analytical techniques are almost impossible due to sample perturbations that may occur during sampling, sample handling and storage. Sample perturbation includes contamination of trace metals or their losses by adsorption onto the wall of containers, but also for samples collected at depths, speciation changes due to variations in temperature, pressure, CO₂ and O₂ content and therefore pH (see Tercier-Waeber and Taillefert 2008; Tercier-Waeber et al., in preparation; for detailed discussion and examples). During the MIR campaign, the VIP system was installed at the side of the MIR submarine, and the end of its sampling tube was fixed to the arm of the submarine (Fig. 1b) to allow in situ Me_{dyn} SWASV measurements in overlying waters sampled at 20 and 40 cm above the sediments. During the boat survey, on-board Me_{dyn} SWASV VIP measurements were performed in an aliquot of the overlying water immediately after sediment core retrieval. SWASV conditions used in both applications were as follows: $E_{dep} = -1,200$ mV; $t_{dep} = 15-30$ min; $E_f = +100$ mV; $f = 200$ Hz; step amplitude 8 mV; pulse amplitude 25 mV. Under these conditions, GIME-VIP analytical limits of detection (LD = blank + 3σ) were 0.9 ng L⁻¹ for Cd, 1.5 ng L⁻¹ for Pb and 10 ng L⁻¹ for Cu. Relative standard deviation (RSD) of the average of 3 replicate measurements was found to be typically ≤ 12 % for concentrations close to the LD and ≤ 8 % for concentrations 3 times the LD.

Analytical methods for chemical analysis in the laboratory

Concentrations of Cd, Pb, Cu and Mn in the samples of overlying (Me_T , Me_D) and interstitial (Me_I) waters, and the digested sediment samples (Me_P) were measured by ICP-

MS (Agilent 7700) using rhodium and rhenium as internal standards. The accuracy of Cd, Pb, Cu and Mn analyses was, respectively, within 6, 3, 3 and 2 % of the certified values of the reference water SLRS-4 ($n = 16$) and precision was generally better than, respectively, 7, 7, 5 and 4 % (RSD; $n = 16$), for concentrations three times higher than detection limits (Cd 0.7 ng L⁻¹, Pb 4 ng L⁻¹, Cu 6 ng L⁻¹, Mn 40 ng L⁻¹; 3σ). Concentrations of the various Fe fractions were measured by GF-AAS (Varian, AA240FS). Accuracy was within 8 % of certified values (SLRS-4) and the analytical error was <5 % at concentrations levels ten times higher than detection limits (GF-AAS 0.5 $\mu\text{g L}^{-1}$; 3σ). Accuracy of Cd_P, Pb_P, Cu_P, Mn_P and Fe_P analyses in certified reference sediment (LKSD-4) digested samples was within 6 % of certified values ($n = 8$) and the analytical error was generally <6 % (RSD; $n = 8$) for all analytes at concentration levels ten times higher than detection limits (Cd 0.02 mg kg⁻¹, Pb 1 mg kg⁻¹, Cu 0.4 mg kg⁻¹, Mn 3 mg kg⁻¹, Fe 0.2 g kg⁻¹; 3σ estimated from blank analyses and for a nominal sample weight of 30 mg of sediment; $n = 8$). POC contents were determined using a CHN analyzer (CHNEA110, CE Instruments Ltd) after carbonate fumigation exposing the particle samples to concentrated HCl vapors for 6 h (Harris et al. 2001).

Results and discussion

Particulate trace metal concentrations in sediments

Concentrations of metals in particulate form (Me_P) in the 3 layers (0–1.5, 1.5–3 and 3–6 cm) of the sediment are reported in Table 2 for the 12 sites. Cd_P, Pb_P and Cu_P concentrations between sites varied in the range 0.86–13.2, 47.6–491 and 92.8–352 mg kg⁻¹, respectively. Me_P concentrations in the three layers at a given site varied by a factor of 1–2 (Table 2). No systematic variation of Me_P concentrations was observed as a function of sediment depth. To compare Me_P concentration levels between the different sites, mean concentrations of the three layers (0–6 cm) were calculated (Fig. 2a). At all sites, mean Cd_P, Pb_P and Cu_P concentrations were higher than the Me_P background concentration level (Arbouille et al. 1989; Cd 0.2 mg kg⁻¹, Pb 30 mg kg⁻¹, Cu 30 mg kg⁻¹) measured in a core collected in the reference station SLH2 in the deepest part of the lake (Fig. 1). Enrichment factors were typically in the range of 5–50, 2–13 and 4–10, for Cd, Pb and Cu, respectively. The Me_P monitored concentrations were compared with threshold effect concentrations (TEC, MacDonald et al. 2000; Cd 0.99 mg kg⁻¹, Pb 35.8 mg kg⁻¹, Cu 31.6 mg kg⁻¹) and the probable effect concentration (PEC, MacDonald et al. 2000; Cd

4.98 mg kg⁻¹, Pb 128 mg kg⁻¹, Cu 149 mg kg⁻¹). For concentrations under the TEC level, toxicity to benthic-dwelling organisms are predicted to be unlikely. For concentrations above the PEC level, toxicity is probable. Between TEC and PEC levels, toxic effects may depend on the type of organism. All Pb_P and Cu_P concentrations and 80 % of the Cd_P concentrations exceeded the TEC. Cu_P concentrations measured at 8 of the 12 sites were higher than the PEC, while higher Cd_P and Pb_P concentrations compared to PEC were measured only at site D and at sites A and D, respectively (Fig. 2a). These results confirm that surface sediments of Vidy Bay are contaminated by the three metals with, for Cu, a probable toxic effect for the biota. Me_P concentrations measured in this study (2011–2012) were, respectively, similar and lower compared to those reported for the years 2005 and 1996; i.e. after and prior the elongation of the WWTP pipe (Poté et al. 2008). This confirms that elongation of the WWTP pipe outlet in an attempt to decrease the impact of metals released by the sewage effluent on sediment quality, i.e. via an increase in their dilution, has been only partially successful. It also suggests that the amounts of metals not retained during the cleaning treatment cycles are at similar level over at least the last decade.

Mean Me_P concentrations measured at site D were superior to those measured at the other sites (Fig. 2a). Site D also was characterized by a high POC concentration (Table 2), the presence of white filament-like bacteria at the sediment surface (Table 1) and important communities of *Beggiatoa* sp. and endospore-forming bacterium *Clostridium* spp. (Sauvain et al. 2013). The latter (~50 % of the total bacterial community; Sauvain et al. 2013) are found in human feces. These results suggest that metals, POC and endospore-forming bacteria observed at site D derive most probably from the WWTP effluent and were co-transported from the outlet pipe to this particular site. Site D is located in a south-west direction from the outlet pipe where an oblate distribution pattern of trace metal in the sediment was observed by Pardos et al. (2004) before the extension of the pipe in 2001. Considering a sedimentation rate of 1–2 cm year⁻¹ in this area (Loizeau et al. 2003), the high Me_P concentrations at site D are unlikely due to metal accumulation prior to 2001 (i.e. prior to extending the pipe). This suggests that a south–west distribution pattern of the metals in the sediment may still be important. This hypothesis is supported by the results of the 3D seasonal monitoring of the WWTP effluent spreading in the water column of Vidy Bay obtained in a recent study that showed a complex spreading pattern of the effluent, although either in a south–west or south–east direction depending on the wind regime (Masson et al., in preparation). These latest results explain not only the high Cd_P and Pb_P concentrations observed at sites A, B, C, D and F but

also at site L (Figs. 1, 2a). They also support the hypothesis that Cd and Pb are mainly issued from the WWTP effluent. The trend in Cu_P concentration distribution appeared slightly different from those of the two other metals, with high Cu_P concentrations measured also at sites I, J and K (Fig. 2a). This suggests an additional diffuse source of Cu_P in the coastal area, possibly from the Chambonne River (another source of water in the bay), in which the watershed drains agricultural regions, including vineyards. This river is also suspected to be the source of some pesticides detected in the bay (Bonvin et al. 2011). Me_P concentrations measured at site D in particular, but also at sites A, B, C, F and L (Fig. 2a), show that the spatial distribution of metal concentrations in the sediments of Vidy Bay is not clearly concentric from the outlet pipe of the WWTP discharge as suggested by Poté et al. (2008) and suggests that the impact of the WWTP effluent is highly variable in space and time (see Goldscheider et al. 2007).

Trace metal in the interstitial water of the sediment

Dissolved Cd, Pb and Cu concentrations measured in the interstitial water (Me_I) of the 3 layers of sediment (0–1.5, 1.5–3 and 3–6 cm) and at the 12 sites varied between 2.8 and 368, 45 and 9,620, 261 and 21,000 ng L⁻¹, respectively (Table 2). Me_I concentrations were generally higher in the deepest layer (3–6 cm) than the two surface layers (0–1.5 and 1.5–3 cm), suggesting differences in bacterial abundance, activities and type, or redox conditions at the three depths. High-resolution profiles of master bio-physicochemical conditions would be required for a more detailed interpretation of the change in metal concentrations monitored in the three layers. As such data are not available at the present state of this work, mean concentrations of the three layers also were compared between sites (Fig. 2b). Mean Cd_I, Pb_I and Cu_I concentrations were clearly higher at site D and at the three closest sites of the pipe outlet, i.e. sites I, J and K (Cd_I 39–180 ng L⁻¹; Pb_I 1,100–4,300 ng L⁻¹; Cu_I 3,970–12,800 ng L⁻¹) compared to those of the other sites (6.3–21, 80–814 and 461–1,560 ng L⁻¹, respectively). These four sites are characterized by the presence of large white filament-like bacterial mats (Table 1) as well as high POC concentrations at sites D and I (Table 2). Therefore, the increase in Me_I for the three target metals is highly suspected to be related to bacterial activity. At sites I, J, and K, mean Fe_I and Mn_I concentrations measured (2,760–6,300 and 70–120 µg L⁻¹, respectively) were also significantly higher than those measured at the other sites (303–3,060 and 22–96 µg L⁻¹, respectively; Table 2). These high Fe_I and Mn_I concentrations highlight a strong reduction of Fe and Mn oxides induced by the important, highly diverse bacterial communities specific to sites I, J and K; i.e. those

closest to the outlet pipe (Sauvain et al. 2013). Similar observations were reported by Haller et al. (2011) in the same area. Bacterial mineralization of organic matter and reduction of Fe and Mn oxides, which are known to be sorbents of choice for the target metals (Dong et al. 2007), may explain the high Cd_I , Pb_I and Cu_I concentrations measured at sites I, J and K (Fig. 2b). The role of bacterial activity on Fe and Mn reduction at sites I, J and K is also supported by the fact that at sites where no bacterial mats were observed, Fe_I and Mn_I concentrations were very low while Fe_P and Mn_P concentrations at all sites were similar (Tables 1, 2). In contrast, at site D, also characterized by high Me_I concentrations of the three target metals (Fig. 2b) and the presence of bacteria (Table 1), Fe_I and Mn_I concentrations were low (Table 2). The low Fe_I and Mn_I concentrations can be explained by the fact that *Beggiatoa* sp. and *Clostridium* spp., the two dominant bacterial species at site D (Sauvain et al. 2013), are not Fe and Mn reducing bacteria. Therefore, the increase in Me_I at site D must be driven by specific activities of either *Beggiatoa* sp. or the endospore-forming bacterium *Clostridium* spp. One possible bacterial activity that may explain the high Me_I concentrations at site D is sulfide oxidation by *Beggiatoa* sp. (Hagen and Nelson 1997) and therefore a decrease in the amount of metals bound to S(II) forming particulate MeS inert complexes (e.g. Zwolsman et al. 1997). More detailed studies are required to better understand the role of these bacteria on metal speciation.

Trace metal speciation in the overlying water

Cd_T , Pb_T and Cu_T concentrations measured in the overlying water varied between 7.4 and 69, 94 and 2,050, and 872 and 4,000 $ng\ L^{-1}$, respectively (Fig. 2c). All Me_T concentrations were higher than the Me_T background concentration level measured at the SLH2 station (3.6, 80, and 712 $ng\ L^{-1}$). The range of Cd_D , Pb_D and Cu_D concentrations was 3.2–8.1, 36–224 and 142–548 $ng\ L^{-1}$ (Fig. 2e). These values are comparable to the Me_D background concentration level (3.3, 41, and 471 $ng\ L^{-1}$). Finally, Cd_{dyn} , Pb_{dyn} and Cu_{dyn} concentrations varied between 1.1 and 6.7, 2.1 and 9.9, 10 and 33 $ng\ L^{-1}$, respectively (Fig. 2f). These concentrations were found to be higher than the Me_{dyn} background concentration level (0.2–0.3, 1.4–1.6, and 0.9–1.1 $ng\ L^{-1}$) monitored in situ with a VIP at station SLH2 (25 m depth). Me_T and Me_D concentrations at sites D and I to K, i.e. where the highest Me_I concentrations were measured, were not higher relative to the other sites (Fig. 2b, c, e). This suggests that the diffusion of dissolved metal from the sediments to the overlying water is negligible, and therefore that the sediments of Vidy Bay act mainly as a sink for trace metals released by the WWTP effluent.

In the overlying water, metal speciation, based on the particulate (Me_{part} : difference between Me_T and Me_D concentrations), colloidal (Me_{coll} : difference between Me_D and Me_{dyn} concentrations) and dynamic fractions, was found to be significantly different, within the analytical errors, from one metal to another at a given site and between the various sites for a given metal (Fig. 3). The proportions of the Cd_{dyn} fraction, i.e. the ratio of the Cd species potentially bioavailable (e.g. Buffle and Tercier-Waeber 2005) to the total Cd concentration, were found to vary as a function of surface sediment characteristics; i.e. <10 % in the overlying water of the sediments covered by white filament-like bacteria; 15–30 % at sites with high and low methanogenic activity; >45 % at sites without bacterial mats and methanogenic activity (Fig. 3). The proportion of the Cu and Pb dynamic species was found to be low (≤ 5 %) at all sites (Fig. 3). These low Cu_{dyn} and Pb_{dyn} proportions, compared to the Cd_{dyn} proportions, are in good agreement with the binding strength of the target metals on natural colloids determined from the ratio of GIME Me_{dyn} to Me_D in freshwater samples stepwise acidified at pH 8–2 (Buffle and Tercier-Waeber 2005). The proportions of the Cu_{dyn} fraction were generally lower in the presence of bacterial mats (<1 %) than in absence of bacterial mats (1–4 %). No clear relationship between Pb_{dyn} and the surface sediment characteristics was observed. Decreases in both Cd_{dyn} and Cu_{dyn} suggest that a significant fraction of these metal species is either assimilated by bacterial communities or complexed by their exudates as non-labile or non-mobile species, or both (Tercier-Waeber et al. 2009; Simon et al. 2011). The role of biota is supported by the fact that Pb_{dyn} , which is known to be not easily assimilated, does not show the same trends. The proportions of the Cd_{coll} and Pb_{coll} fractions were also different as a function of the surface sediment characteristics; i.e. respectively 0 and 4 % at sites with high methanogenic activity, 2–25 and 10–20 % at sites characterized by bacterial mats, 20–50 and 35–75 % at sites without bacterial mats and methanogenic activity (Fig. 3). For Cu, no changes in the proportions of colloidal species were observed in the presence or absence of bacterial mats at the sediment surface (Fig. 3). Considering that at the level of metal concentrations measured in the overlying water, Cd and Pb are expected to be bound mainly to inorganic colloids (e.g. Mn and Fe (hydrated-)oxides) while Cu is mainly complexed to organic matter (Dong et al. 2007), one hypothesis that may explain the decrease of Cd_{coll} and Pb_{coll} at the site characterized by bacterial communities is the hetero-aggregation of inorganic colloids resulting from their bridging by extracellular polymeric substances (Tercier-Waeber et al. 2012). More detailed studies coupling trace metal speciation with characterization of colloidal and particulate matter at the

Table 2 Concentrations of Cd, Pb, Cu, Fe and Mn adsorbed in the sediment (Me_P ; in $mg\ kg^{-1}$) and measured in the interstitial water (Me_I ; in $ng\ L^{-1}$) for the three sampled layers (0–1.5, 1.5–3, 3–6 cm); concentrations of Cd, Pb, Cu, Fe total (Me_T), dissolved (Me_D) and dynamic (Me_{dyn}) fractions measured in the overlying water (in $ng\ L^{-1}$); and POC concentrations measured in the sediment

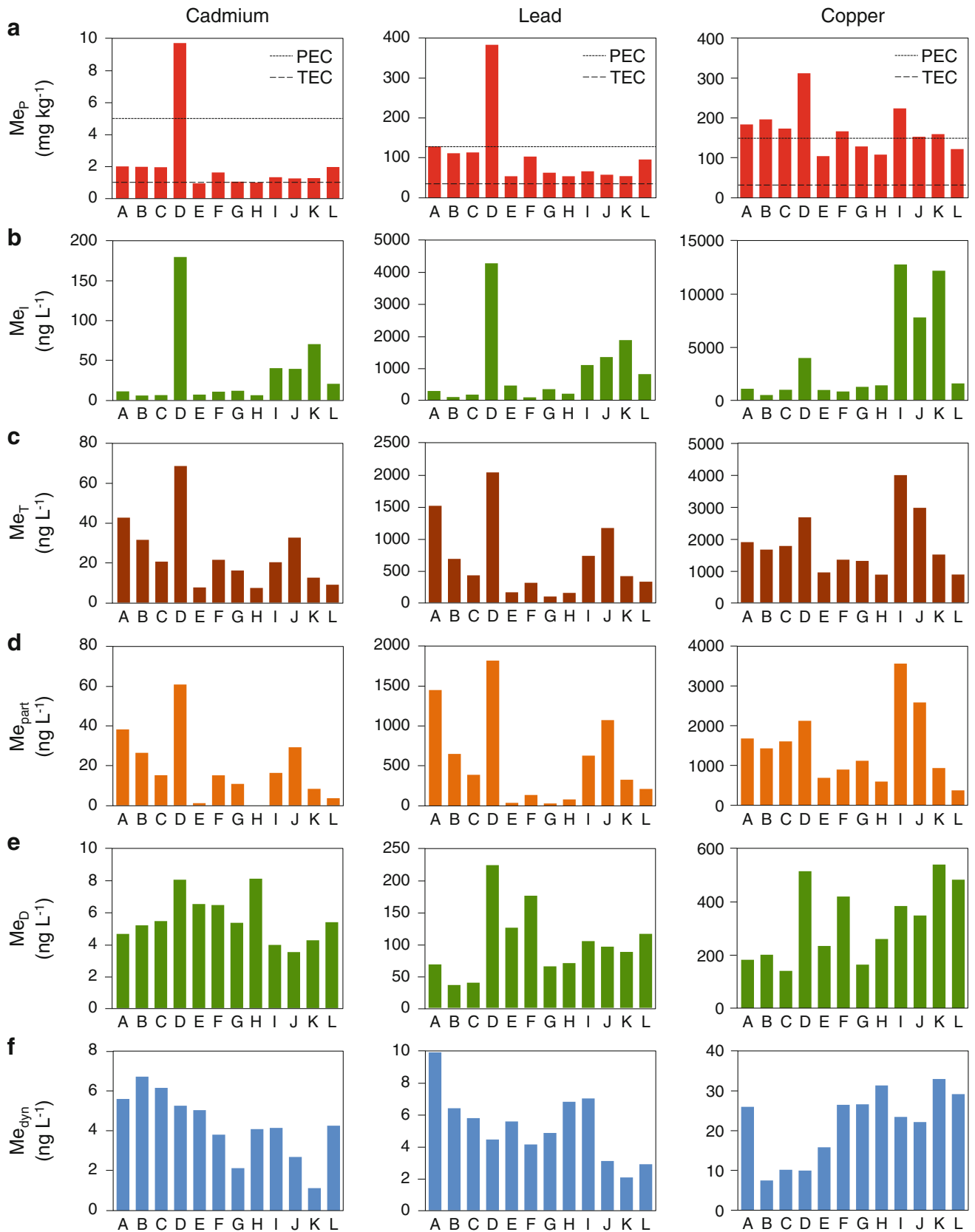
Sed. int./o.w.	Cd $mg\ kg^{-1}$ $ng\ L^{-1}$	Pb $mg\ kg^{-1}$ $ng\ L^{-1}$	Cu $mg\ kg^{-1}$ $ng\ L^{-1}$	Fe $g\ kg^{-1}$ $\mu g\ L^{-1}$	Mn $g\ kg^{-1}$ $\mu g\ L^{-1}$	POC (%)
A						
Me_P 0–1.3 cm	1.84	120	179	35.8	0.389	4.3
Me_P 1.5–3 cm	1.58	101	160	33.6	0.395	
Me_P 3–6 cm	2.62	169	218	34.4	0.425	4.5
Average	2.01	130	185	34.6	0.403	4.4
Me_I 0–1.5 cm	7.2	45	1,190	25.6	2.59	
Me_I 1.5–3 cm	6.9	182	326	2,150	59.0	
Me_I 3–6 cm	19	623	1,660	6,990	20.7	
Average	11	283	1,060	3,060	27.4	
Me_T	43	1,520	1,890	11.3	17.5	
Me_D	4.6	68	185	9.24	13.4	
Me_{dyn}	5.6	10	26			
B						
Me_P 0–1.5 cm	1.91	119	203	35.5	0.378	4.5
Me_P 1.5–3 cm	1.99	104	192	36.7	0.403	
Me_P 3–6 cm	2.06	115	199	35.2	0.407	3.9
Average	1.98	112	198	35.8	0.396	4.2
Me_I 0–1.5 cm	7.2	171	536	542	46.0	
Me_I 1.5–3 cm	2.9	51	396	436	55.0	
Me_I 3–6 cm	7.3	54	450	1,150	74.7	
Average	5.8	92	461	709	58.6	
Me_T	32	686	1,660	6.92	16.4	
Me_D	5.2	36	204	10.2	11.0	
Me_{dyn}	6.7	6	8			
C						
Me_P 0–1.5 cm	2.77	151	182	31.1	0.349	4.4
Me_P 1.5–3 cm	1.53	95.4	166	32.4	0.361	
Me_P 3–6 cm	1.59	97.3	177	31.7	0.374	4.2
Average	1.96	115	175	31.7	0.361	4.3
Me_I 0–1.5 cm	5.8	186	655	176	35.4	
Me_I 1.5–3 cm	3.6	95	261	224	46.0	
Me_I 3–6 cm	9.9	226	1,970	2,360	73.0	
Average	6.4	169	962	920	51.5	
Me_T	21	428	1,770	13.0	21.2	
Me_D	5.4	39	142	12.3	16.6	
Me_{dyn}	6.2	6	10			
D						
Me_P 0–1.5 cm	5.84	247	258	42.9	0.345	7.0
Me_P 1.5–3 cm	10.2	418	333	53.4	0.367	
Me_P 3–6 cm	13.2	491	352	52.3	0.396	7.7
Average	9.77	386	314	49.5	0.369	7.4
Me_I 0–1.5 cm	22.8	239	1,190	252	6.71	
Me_I 1.5–3 cm	149	3,050	4,610	621	13.5	
Me_I 3–6 cm	368	9,620	6,110	732	45.3	
Average	180	4,300	3,970	535	21.9	
Me_T	69	2,050	2,680	7.99	23.7	
Me_D	8.0	224	523	21.2	15.8	
Me_{dyn}	5.3	4	10			

Table 2 continued

Sed. int./o.w.	Cd mg kg ⁻¹ ng L ⁻¹	Pb mg kg ⁻¹ ng L ⁻¹	Cu mg kg ⁻¹ ng L ⁻¹	Fe g kg ⁻¹ µg L ⁻¹	Mn g kg ⁻¹ µg L ⁻¹	POC (%)
E						
Me _P 0–1.5 cm	0.990	58.8	107	29.6	0.394	
Me _P 1.5–3 cm	0.980	56.5	117	31.1	0.415	4.1
Me _P 3–6 cm	0.859	48.3	92.8	32.2	0.475	3.3
Average	0.943	54.5	106	31.0	0.428	3.7
Me _I 0–1.5 cm	3.6	264	374	62.5	52.3	
Me _I 1.5–3 cm	4.9	428	779	211	55.2	
Me _I 3–6 cm	13	666	1,700	635	47.3	
Average	7.0	453	951	303	51.6	
Me _T	7.7	161	941	8.77	15.6	
Me _D	6.5	125	237	10.8	11.4	
Me _{dyn}	5.1	6	16			
F						
Me _P 0–1.5 cm	1.37	85.7	151	31.2	0.399	4.0
Me _P 1.5–3 cm	1.31	85.0	148	31.3	0.377	
Me _P 3–6 cm	2.22	141	205	32.2	0.378	5.1
Average	1.63	104	168	31.5	0.385	4.5
Me _I 0–1.5 cm	11	125	356	266	27.3	
Me _I 1.5–3 cm	7.2	54	630	443	28.5	
Me _I 3–6 cm	14	60	1,430	644	55.3	
Average	11	80	805	451	37.0	
Me _T	22	311	1,340	11.3	15.0	
Me _D	6.5	176	426	11.1	9.08	
Me _{dyn}	3.8	4	27			
G						
Me _P 0–1.5 cm	1.00	58.4	133	31.0	0.411	3.7
Me _P 1.5–3 cm	1.04	64.2	130	31.0	0.405	
Me _P 3–6 cm	1.13	67.3	127	31.4	0.405	3.6
Average	1.06	63.3	130	31.1	0.407	3.7
Me _I 0–1.5 cm	6.4	149	662	174	42.4	
Me _I 1.5–3 cm	5.9	207	823	206	9.42	
Me _I 3–6 cm	23	669	2,250	916	31.9	
Average	12	341	1,240	432	27.9	
Me _T	16	94	1,300	25.1	22.1	
Me _D	5.3	65	166	7.01	17.5	
Me _{dyn}	2.1	5	27			
H						
Me _P 0–1.5 cm	0.940	47.6	93.0	31.0	0.441	3.3
Me _P 1.5–3 cm	0.998	51.9	106	34.1	0.486	
Me _P 3–6 cm	1.04	64.0	130	29.8	0.390	2.9
Average	0.99	54.5	110	31.7	0.439	3.1
Me _I 0–1.5 cm	5.4	151	1,160	532	67.8	
Me _I 1.5–3 cm	2.8	62	584	1,040	96.1	
Me _I 3–6 cm	11	375	2,390	1,510	123	
Average	6.3	196	1,380	1,030	95.7	
Me _T	7.4	150	872	7.33	21.4	
Me _D	8.1	70	264	7.38	16.2	
Me _{dyn}	4.1	7	31			

Table 2 continued

Sed. int./o.w.	Cd mg kg ⁻¹ ng L ⁻¹	Pb mg kg ⁻¹ ng L ⁻¹	Cu mg kg ⁻¹ ng L ⁻¹	Fe g kg ⁻¹ μg L ⁻¹	Mn g kg ⁻¹ μg L ⁻¹	POC (%)
I						
Me _P 0–1.5 cm	1.31	98.3	205	40.2	0.334	12.6
Me _P 1.5–3 cm	1.36	53.3	219	51.2	0.348	13.2
Me _P 3–6 cm	1.33	49.6	253	64.4	0.324	10.1
Average	1.33	67.1	226	51.9	0.335	12.0
Me _I 0–1.5 cm	28	886	8,850	5,870	78.3	
Me _I 1.5–3 cm	50	1,350	15,800	2,700	55.8	
Me _I 3–6 cm	43	1,060	13,800	10,300	117	
Average	40	1,100	12,800	6,290	83.6	
Me _T	20	734	4,000	820	8.40	
Me _D	4.0	104	390	45.7	6.31	
Me _{dyn}	4.2	7	24			
J						
Me _P 0–1.5 cm	1.23	54.4	161	39.3	0.388	4.7
Me _P 1.5–3 cm	1.21	59.0	139	39.4	0.403	4.7
Me _P 3–6 cm	1.33	61.0	164	47.1	0.379	4.3
Average	1.26	58.13	154	42.0	0.390	4.6
Me _I 0–1.5 cm	22	695	5,310	3,930	80.8	
Me _I 1.5–3 cm	36	1,330	6,160	3,740	97.0	
Me _I 3–6 cm	60	2,030	11,900	8,110	183	
Average	39	1,350	7,790	5,260	120	
Me _T	33	1,170	2,980	546	6.71	
Me _D	3.5	96	354	19.1	4.92	
Me _{dyn}	2.7	3	22			
K						
Me _P 0–1.5 cm	1.27	48.9	179	42.6	0.367	4.3
Me _P 1.5–3 cm	1.19	53.8	145	39.2	0.412	4.4
Me _P 3–6 cm	1.36	61.5	158	49.5	0.421	4.0
Average	1.27	54.7	161	43.7	0.400	4.2
Me _I 0–1.5 cm	29	935	6,080	1,680	38.7	
Me _I 1.5–3 cm	54	1,550	9,550	1,580	59.3	
Me _I 3–6 cm	128	3,160	21,000	5,030	112	
Average	71	1,880	12,200	2,760	69.9	
Me _T	13	414	1,500	166	3.00	
Me _D	4.2	88	548	18.6	1.29	
Me _{dyn}	1.1	2	33			
L						
Me _P 0–1.5 cm	1.92	83.1	120	26.4	0.381	4.0
Me _P 1.5–3 cm	1.70	84.9	116	28.9	0.399	4.8
Me _P 3–6 cm	2.30	122	134	31.4	0.410	4.0
Average	1.97	96.8	123	28.9	0.397	4.2
Me _I 0–1.5 cm	10	353	1,010	231	32.0	
Me _I 1.5–3 cm	10	315	765	192	33.6	
Me _I 3–6 cm	41	1,770	2,910	1,960	68.5	
Average	21	813	1,560	794	44.7	
Me _T	9.0	327	875	63.3	1.93	
Me _D	5.4	116	491	17.0	1.25	
Me _{dyn}	4.3	3	29			



◀ **Fig. 2** Mean Cd, Pb and Cu concentrations determined from concentrations measured in the three layers (0–1.5, 1.5–3, 3–6 cm) of the sediment (**a** Me_p) and of the overlying water (**b** Me_l). Concentrations of the Cd, Pb and Cu total (**c** Me_T), particulate (**d** Me_{part}), total dissolved (**e** Me_D) and dynamic (**f** Me_{dyn}) fractions measured in the overlying water

various sites are required to verify this hypothesis. Finally, the Me_{part} proportions of the three metals were generally higher at all sites characterized by methanogenic activity (Fig. 3). This may be explained by a resuspension of Me_p in the overlying water due to intense methane degassing. The increase in suspended particulate matter, favoring the adsorption/aggregation of colloidal metal species, may also explain the low contributions of Cd_{coll} and Pb_{coll} at these sites (Fig. 3).

Summary and outlook

For the first time, speciation of Cd, Pb and Cu in addition to total metal concentrations were investigated at the sediment–water interface of Vidy Bay. This work was a first attempt to evaluate the potential impact of contrasting sediment characteristics on trace metal speciation in both compartments. Several interesting findings were obtained: (1) the study confirmed that the elongation of the outlet pipe releasing WWTP sewage effluent has not solved the problem of contamination of sediments by trace metals not retained during water treatment. (2) The differences in trace metal concentrations and speciation at the sediment–water interface were found to be more related to sediment bacterial abundance, activity and types than to the distance from the outlet pipe. (3) Bacterial activity was found to influence the speciation of the three metals in the sediment and overlying water via processes that depend on the

abundance and type of bacterial community. Increase in dissolved metal concentrations in the interstitial water (Me_l) was attributed to organic matter mineralization, Fe/Mn oxide reduction and sulfide oxidation. Methanogenic activity induces resuspension of metal in particulate form (Me_p) from the sediment to the overlying water. Bacterial activity is also suspected to be at the origin of the changes in the proportion of dynamic (Me_{dyn}) and colloidal (Me_{coll}) metal species in the overlying water. (4) Finally, the results of this study suggest that the sediments act mainly as a sink for the metals released by the WWTP effluent; the only identified exception being related to the Me_p resuspension induced by methane degassing. Findings 2–4 could not be obtained from measurements of only metal in the particulate form in the sediments as performed in the previous studies. They highlight the interest and potential of the proposed analytical approach coupling visual observation of sediment characteristics with combined in situ and laboratory measurements of metal concentrations and speciation in the different compartments (i.e. sediment, interstitial and overlying waters) to study the behavior and fate of trace metals at the sediment–water interface and identify the processes that may control them.

More detailed spatial and temporal studies coupling high-resolution chemical measurements (trace metal speciation, redox compounds, major ion concentrations, colloidal and particulate matter characterization) to microbiological characterization are still needed. This is a pre-requisite condition to investigate in depth the feedback interactions between trace metal speciation and bacterial community, and the way for more reliable evaluation of the behavior and fate of trace metals released by the WWTP effluent, and assessment of their long-term impact on the Vidy Bay ecosystem.

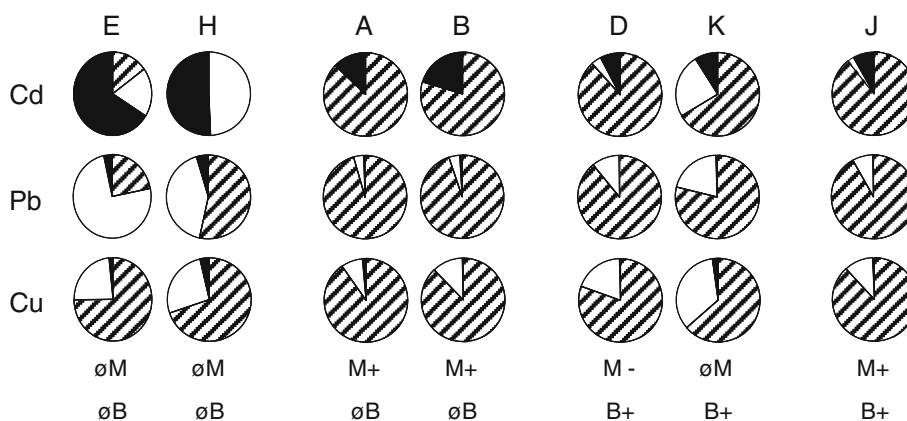


Fig. 3 Proportion of the Cd, Pb and Cu particulate (*hatched area*), colloidal (*white area*) and dynamic (*black area*) fractions to the total metal concentration measured in the overlying water at selected sites characterized by absence of methanogenic activity and bacterial mat

(sites *E, H*), high methanogenic activity and absence of bacterial mat (sites *A, B*), absence or low methanogenic activity and presence of large bacterial mat (sites *D, K*), and high methanogenic activity and presence of large bacterial mat (site *J*)

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