

## **Sediment–contaminant interactions and transport: a new perspective**

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**Abstract** This paper investigates the sediment structural controls over the transport and compartmentalization of Cd, Cu and Pb within flocculated sediments. The compartmentalization of contaminants within flocculated sediment particles demonstrates the complex underlying biogeochemical controls of sediment contaminant interactions. The aims and objectives of the paper are to demonstrate (a) how the structure of suspended sediment particles will influence the transfer of metals within aquatic systems and (b) how the internal structure/composition of the particles promotes compartmentalization of metals in a selective manner.

**Key words** bacteria; Cd; clay; Cu; EPS; flocc; flocculation; metals; Pb

### **INTRODUCTION**

Sediment transport and sediment contaminant interactions are often diagnosed using bulk sediment/contaminant loads. Such loading estimates are useful for the identification of basin disturbances, trend assessments, receiving water body loadings (infilling rates) and for the general management of water systems. Our understanding of how the sediment structure influences the transport of this sediment and how and where contaminants are compartmentalized within the sediment particles (flocs) is, however, poorly understood. This paper reports results from various image analysis techniques, microscopy and sequential metal extraction for the assessment of how sediment structure influences sediment and contaminant transport and provides insight into the complex interaction of metals with various components of flocculated sediment particles. A better understanding of these relationships will further our ability to predict the source, fate, and effect of sediments and contaminants within aquatic systems, thus facilitating more effective management decisions.

### **METHODS**

#### **Sample sites**

Suspended and bed sediment samples were collected from Hamilton Harbour near the outfall of Red Hill Creek/Windermere Basin (RHWB) and Grindstone Creek (GC). The geology of both creeks is similar (Ongley, 1974). The primary difference is that GC is primarily a rural catchment while RHWB drains a large area of urban and industrial land. In addition RHWB is also the receiving water body for the main Hamilton sewage treatment plant (STP) and receives multiple combined sewer overflows during storm conditions. As such the organic content of RHWB is substantially higher and has a characteristic sewage odour. Five additional sites, distributed throughout the harbour, were used for bed sediment collection.

## Sediment sampling and analysis

Recently deposited surficial fine-grained laminae (SFGL) (Droppo & Stone, 1994) were collected by scraping the top few mm of sediment from a 50 cm<sup>2</sup> box core. These bulk samples were used for sequential extraction metals analysis following the method of Tessier & Campbell (1988). This method allows for the assessment of the partitioning of metals according to the categories exchangeable, bound to carbonates, bound to Fe/Mn oxides, bound to organics and held within the crystalline structure of the sediment. These fractions can be viewed as a gradient of decreasing bioavailability, with the residual fraction not being bioavailable. In our assessment, exchangeable and carbonate fractions were combined.

Suspended floc samples for structural and compositional analysis were sampled following the method of Droppo *et al.* (1997) which incorporates the use of plankton chambers. Disturbance of the flocs is minimized by the plankton chambers functioning as both the sampling instrument and the analytical cell for laboratory observation and measurement.

A 12 l water/suspended sediment sample was used for determination of floc settling velocity, density and porosity following the settling image analysis technique described in Droppo *et al.* (1997). Further sub-samples were used for correlative microscopic analysis following the methods of Liss *et al.* (1996). Correlative microscopy here entails the use of conventional optical (COM), environmental scanning electron (ESEM) and transmission electron microscopy (TEM) being applied to the same sample (Leppard *et al.*, 2003). The TEM was equipped with energy dispersive spectroscopy (EDS) for the identification of metal associations with submicrometer entities of the floc. The reader is referred to the above publications for detailed descriptions of these techniques.

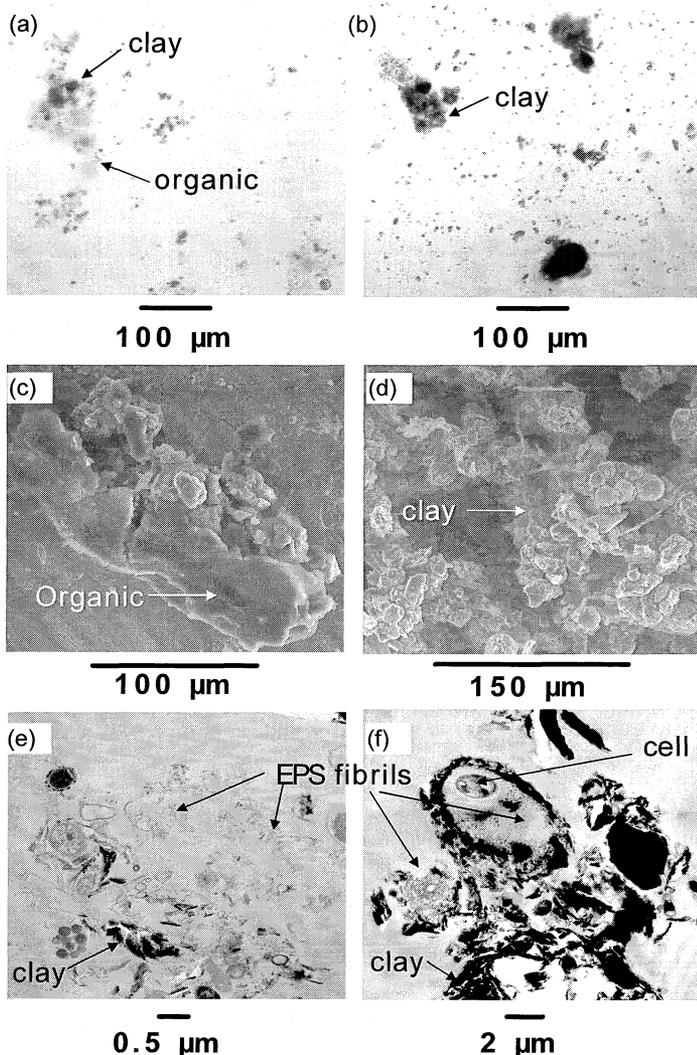
## RESULTS AND DISCUSSION

Flocs were characterized, with regard to principal structural, chemical, and microbiological components and properties, in relation to metal contaminant–particle/colloid associations and floc settling as a surrogate of sediment transport.

### Principal floc structure and composition—gross and fine

The structure of flocs is discussed here to illustrate their complex nature and the multiple binding sites for metals. Figure 1 illustrates the substantive differences between sample site flocs with representative micrographs for COM (Fig. 1(a),(b)), ESEM (Fig. 1(c),(d)), and TEM (Fig. 1(e),(f)) analysis. It is evident that both floc samples possess irregular shaped particles with open matrices composed of both organic and inorganic particles (Fig. 1). RHWB flocs were much more organic and diffuse in appearance compared to the GC flocs which were composed of more inorganic matter (Fig. 1(a),(b)). Many of the RHWB flocs had an amorphous organic coating (Fig. 1(c)), compared to the more mineral contact of the GC flocs (Fig. 1(d)). Loss-on-ignition (LOI) analysis of respective bed sediments also revealed that the RHWB sediment had an organic content 3 times higher than the GC sediments (Table 1). The internal structure of the both floc samples (Fig. 1(e),(f)) can be described as tortuous. Multiple convoluted channels are defined by the constituent particles

of clay minerals, bacterial cells, residues of bacterial cell walls, granules, higher level organisms such as diatoms and the colloidal particles of extracellular polymeric substances (EPS) manifested as fibrillar material (Fig. 1(e),(f)). The TEM micrographs illustrate the large degree of EPS associated with the floc matrix and pores for both floc samples, but to a higher degree within the RHWB flocs. This EPS increases the cohesiveness of the floc thus promoting further flocculation, provided that shear conditions are favorable. It maintains a high porosity within both flocs and with the EPS fibrils being colloidal in size they induce high surface tensions and water retention. In addition, EPS is believed to be largely responsible for floc strength, with EPS densities observed to be the greatest in the centre of the floc and diffusing outwards (Droppo *et al.*, 1997; Liao *et al.*, 2002). Such an EPS



**Fig. 1** Representative micrographs of RHWB (a, c and e) and GC (b, d and f) sample site flocs using three different microscopes: COM (a and b), ESEM (c and d) and TEM (e and f).

**Table 1** Characteristics of flocs and bed sediment samples collected at stations.

	Grindstone Creek	Red Hill Creek–Windermere Basin
LOI (%)	7.6	23.0
% Sand	2.3	3.1
% Silt	67.1	61.5
% Clay	30.6	35.4
Mineralogy	Quartz, Calcite/Dolomite, Feldspars & Goethite	Quartz, Calcite/Dolomite, Feldspars & Goethite
Dominant clay mineral	Mica>Kaolinite>Chlorite	Mica>Kaolinite>Chlorite
D <sub>50</sub> sonicated (µm)	6.1	7.8
d <sub>50</sub> floc (µm)	119.0	188.0
Mean settling velocity (mm s <sup>-1</sup> )	3.08 ± 1.92	1.75 ± 0.56
Mean floc density (g cm <sup>-3</sup> )	1.12 ± 0.06	1.05 ± 0.04
Mean porosity (%)	81.7 ± 9.7	92.6 ± 7.1

± standard deviation; Greater than 5000 particles analysed for particle size distributions, 102 particles analysed for settling velocity, density and porosity.

gradient is suggestive of a strong core with a high potential of surficial floc growth in addition to chemical transport within the floc being likely related to diffusional and electrochemical gradients (due to high density EPS micro pore structure) (Droppo, 2001).

Both sites had similar mineralogy and inorganic grain size characteristics (Table 1) with floc size by-volume distributions negatively skewed and by-number distributions positively skewed. As such, the larger floc sizes represent the majority of the mass for the samples but the majority of the particles were small in size. The RHWB site showed a much larger floc size distribution (Table 1) which is indicative of flocs having a high organic content (Droppo, 2001). Similar floc sizes were found by Droppo *et al.* (2002) for combined sewer flocs.

### Floc structural influence on sediment/contaminant transport

As the majority of sediment is transported as flocs (Droppo, 2001), contaminant transport will be dictated by the size, structure, composition and density characteristics of the flocs themselves. GC flocs had settling velocities which ranged between 1 and 10 mm s<sup>-1</sup> and showed the common relationship of increasing settling velocity with floc size ( $r^2 = 0.68$ ). The RHWB sediments, however, showed no relationship between these two variables with all flocs settling between approximately 3 and 1 mm s<sup>-1</sup>. This poor relationship and lower settling velocity is related to the structure of the RHWB flocs being highly organic and diffuse in nature promoting a consistent low density range (0.002–0.12 g cm<sup>-3</sup>) and minimizing the effects of size on settling. Although the RHWB flocs were generally larger (Table 1), more than half of the RHWB flocs had densities an order of magnitude below those of the GC flocs (density range 0.04–0.14 g cm<sup>-3</sup>). A strong inverse relationship was observed between floc size and density ( $r^2 > 70\%$ ) for both sample sites. As such, one would expect that contaminants associated with RHWB would be transported further than those from GC. Studies of Hamilton Harbour have shown that the entire Windermere arm of the harbour is contaminated with metals, PCBs and PAHs (Zeman & Patterson, 2003). It is likely that this contaminant distribution is controlled, in part, by floc structural influences on sediment/contaminant transport.

## Floc structural influence on floc contaminant characteristics

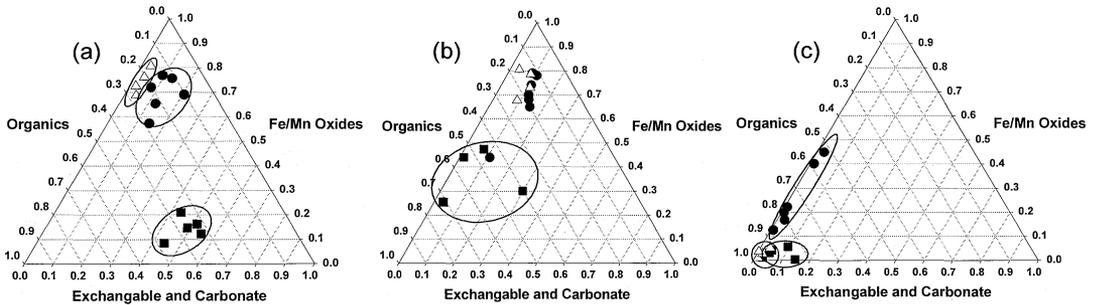
The complexity of a floc's structural, chemical and microbial components and properties will play havoc on any attempt to provide a universal relationship of contaminants to some gross sediment particle property (e.g. size). Unlike traditional mono-structure sediments, flocs have multiple binding sites (Droppo, 2001) which are not static, but which may continually vary the internal metal composition/phase or concentration. Nevertheless, it is evident from the above structural synopsis that some general insights are possible. Clay particles will be active receptors of contaminants; however, it is likely the colloidal fraction of bacterial cells, residues of bacterial cell walls, granules (likely Fe oxides), higher level organisms (such as diatoms) and EPS fibril material will be the dominant surfaces controlling metal behaviour within the flocs due to their small size, relatively great unit surface area, and therefore high reactivity. This will be particularly true for the RHWB flocs which are much higher in organic content.

Recent interdisciplinary studies on flocs support the idea that EPS composition is an important component whose surface properties control hydrophobicity and surface charge at the floc-water interface, while bound water can be a function of floc size and total EPS (Liao *et al.*, 2001, 2002). These properties, as influenced by EPS, all play a role in the flocculation and contaminant interactions of cohesive sediments. Flocs have also been observed to possess anaerobic zones within the core of the floc where EPS densities are usually the highest and oxygen may be depleted (Simon *et al.*, 2002). Such gradients in redox potential may result in the fixation or mobilization of metals within the flocs. Generally an anaerobic zone will promote metal uptake. Ph gradients set up within a floc will also affect the migration of metal ions within the floc matrix through diffusional processes (Warren & Haack, 2001).

## Metal composition—bulk analysis and EDS analysis

Bulk metal analysis provides little insight into the factors that control the transport and interaction of contaminants with/within the sediment particles. Traditional geochemical relationships have demonstrated that as particle size decreases, the potential for contaminant uptake increases. This relationship is, however, based on individual particles and does not reflect the true structure by which sediment and contaminants are transported (i.e. as flocs). While classical metal binding to individual clay particles prior to flocculation occurs, metals may be transformed, relocated within the floc matrix, or added to by the diffusion and electrochemical processes operating within the floc. These processes, in conjunction with microbial metabolism, chemical precipitation and co-precipitation, dissolution and volatilization, are what dictate the dynamic metal concentrations within the floc (see Warren & Haack (2001) for a comprehensive review of biogeochemical controls on metal behaviour).

While it is not feasible to fully understand the complex relationship of floc-metal interactions, sequential extraction (even with its limitations, Tessier & Campbell, 1988) does provide insight into the relative partitioning of metals within the flocs (although still with a bulk sample). A preliminary survey of Hamilton Harbour SFGL (including SFGL from the two study sites), suggest that both Cd and Pb were primarily bound within Fe/Mn oxides



**Fig. 2** Ternary plots of (a) Cd, (b) Pb and (c) Cu for labile fractions only within SFGL (●), street dust (■) and CSO (△) sediments (Residual fraction has been removed, exchangeable and bound to carbonate phase has been combined and the fractions adjusted to 100%).

(60–80%) (Fig. 2). Similar findings have been found for urban sediments and urban impacted rivers by Stone & Marsalek (1996), Droppo *et al.* (1998) and Sutherland & Tack (2000). Fe/Mn oxides are often manifested as precipitated crystalline forms or coatings and often dominate the geochemical reactivity of the sediment component. Microbial activity can further promote Fe/Mn oxides within flocs. These forms of oxides are often smaller and more diffuse than chemical precipitates and as such possess extensive surface areas for metal uptake (Warren & Haack, 2001). The presence of Fe/Mn oxides is substantiated by goethite being present as one of the dominant minerals (Table 1). Goethite is a transformed stable version of ferrihydrite; a common Fe oxide within freshwater (Warren & Haack, 2001). Fig. 2 also plots the data for CSOs and street dust collected within the Kenilworth sewershed which contributes to the RHWB sample site from a previous study (e.g. Droppo *et al.*, 1998; Irvine *et al.*, 1999). Comparison of the overall Hamilton Harbour SFGL data shows that the CSO samples contained similar ratios of the metal phases while the street dust was quite different. This suggests that the sanitary portion of the CSO and three STP discharges may be a significant contributor to the metal characteristics of Hamilton Harbour SFGL. The CSO will deliver street dust to the harbour during washoff and overflow events, but its ratio signature does not correspond with the SFGL samples. Only for Pb does the street dust appear to make a contribution to the SFGL. However, this is only one sample and further work will be required to resolve this issue.

Copper analysis revealed a common association with the organic fraction of the sediment (55–90%) (Fig. 2). This organic fraction is heterogeneous and can include viable or non-viable bacteria, humic and fulvic acids and the colloidal fraction contributed by the extensive EPS network of the flocs and bacteria. Organics are effective scavengers of metals due to their large surface areas and multiple surface functional groups. Small organic molecules are generally more labile and taken individually may have a lower residence time in aquatic systems (Warren & Haack, 2001). However, organic molecules often are adsorbed onto mineral surfaces and when incorporated in flocs, these organic materials contribute to floc building and influence the behaviour of metals (organic coatings can inhibit or enhance metal binding – Warren & Haack, 2001). Bacteria themselves possess surface functional groups and can sorb metal species to their surface although this process could be complicated by the EPS secreted by the bacterium or other substances dissolved in the water (Warren & Haack, 2001; Chatellier *et al.*, 2004). It would appear (Fig. 2) that the phases of

Cu are possibly controlled more by fluvial and erosional processes than by the CSOs or street dust as the data plots in a different area of the graph (although the RHWB sample was closest to the CSO and street dust data points).

Recent assessment of individual binding sites within industrial wastewater flocs using TEM and EDS has revealed considerable insight (Leppard *et al.*, 2003). However, within the present study, only in very limited cases was Cu, Cd or Pb found to be attached to any component of the floc, even though high concentrations were observed with sequential extraction analysis. This lack of data generated by EDS may be related to: (a) concentrations not being high enough for detection to consistently show binding to one specific site, and/or (b) the small sample volume analysed for TEM missing important metal attachment sites. In the Leppard *et al.* (2003) study, although concentrations of metals were orders of magnitude higher than in this study, Pb was found to be preferentially bound to polyphosphate granules. It is possible that a similar relationship is at play for natural sediments, but that concentrations of metal ions on any one surface are not high enough for detection.

## CONCLUSIONS

- (a) Flocculation is a dynamic process which influences the transport and contaminant-binding behavior of suspended sediment.
- (b) Floc characteristics and settling behaviors were very different between the RHWB and GC sites due to significant structural differences (primarily organic differences).
- (c) Colloidal fractions are important binding sites for metals due to their large reactive surface area and therefore high reactivity.
- (d) Cd and Pb were preferentially bound to Fe/Mn oxides while Cu was preferentially bound to organic material. Concentrations were likely not elevated enough for metal spectrum analysis with EDS.

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## REFERENCES

- Chatellier, X., West, M. M., Rose, J., Fortin, D., Leppard, G. G. & Ferris, F. G. (2004) Characterization of iron-oxides formed by oxidation of ferrous ions in the presence of various bacterial species and inorganic ligands. *Geomicrobiol. J.* (in press).
- Droppo, I. G. (2001) Rethinking what constitutes suspended sediment. *Hydrol. Processes* **15**, 1551–1564.
- Droppo, I. G. & Stone, M. (1994) In-channel surficial fine-grained sediment laminae (Part I): Physical characteristics and formational processes. *Hydrol. Processes* **8**, 101–111.
- Droppo, I. G., Leppard, G. G., Flannigan, D. T. & Liss, S. N. (1997) The freshwater floc: A functional relationship of water and organic and inorganic floc constituents affecting suspended sediment properties. *Water Air & Soil Pollut.* **99**, 43–53.
- Droppo, I. G., Irvine, K. N., Murphy, T. P. & Jaskot, C. (1998) Fractionated metals in street dust of a mixed land use sewershed, Hamilton, Ontario. In: *Hydrology in a Changing Environment*, Volume 3 (ed. by H. Wheatler & C. Kirby), 383–394. John Wiley & Sons Ltd., New York, USA.
- Droppo, I. G., Irvine, K. N. & Jaskot, C. (2002) Flocculation of cohesive sediments in the urban continuum: Implications for stormwater management. *Environ. Technol.* **23**, 27–41.
- Irvine, K. N., Droppo, I. G. & Murphy, T. P. (1999) Contaminant levels and loading estimates: The first step in identifying restoration options for a Great Lakes Area of Concern. In: *Aquatic Restoration in Canada* (ed. by T. Murphy & M. Munawar), 51–68. Backhuys Publishers, The Netherlands.
- Leppard, G. G., Droppo, I. G., West, M. & Liss, S. N. (2003) Compartmentalization of metals within the diverse colloidal matrices comprising activated sludge microbial flocs. *J. Environ. Qual.* **32**, 2100–2108.

- Liao, B. Q., Allen, D. G., Droppo, I. G., Leppard, G. G. & Liss, S. N. (2001) Surface properties of activated sludge and their role in bioflocculation and settling: extracellular polymeric substances, hydrophobicity and surface charge. *Water Res.* **35**, 339–350.
- Liao, B. Q., Allen, D. G., Leppard, G. G., Droppo, I. G. & Liss, S. N. (2002) Interparticle interactions affecting the stability of sludge flocs. *J. Coll. Interf. Sci.* **249**, 372–380.
- Liss, S. N., Droppo, I. G., Flannigan, D. T. & Leppard, G. G. (1996) Floc architecture in wastewater and natural riverine systems. *Environ. Sci. Technol.* **30**, 680–686.
- Ongley E. D. (1974) *Hydrophysical Characteristics of Great Lakes Tributary Drainage, Canada*. Pollution and Land Use Activities Reference Group (PLUARG), IJC, Windsor, Canada.
- Simon, M., Grossart, H. -P., Schweitzer, B. & Ploug, H. (2002) Microbial ecology of organic aggregates in aquatic systems. *Aquat. Microb. Ecol.* **28**, 175–211.
- Stone, M. & Marsalek, J. (1996) Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. *Water Air & Soil Pollut.* **87**, 149–169.
- Sutherland, R. A. & Tack, F. M. G. (2000) Metal phase associations in soils from an urban watershed, Honolulu, Hawaii. *Sci. Total Environ.* **256**, 103–113.
- Tessier, A. & Campbell, P. G. C. (1988) Partitioning of trace metals in sediments, In: *Metal Speciation: Theory, Analysis and Application* (ed. by J. R. Kramer & H. E. Allen), 183–199. Lewis, New York, USA.
- Warren, L. A. & Haack, E. A. (2001) Biogeochemical controls on metal behaviour in freshwater environments. *Earth Sci. Rev.* **54**, 261–320.
- Zeman, A. J. & Patterson, T. S. (2003) *Sediment survey of Windermere Arm, Hamilton Harbour*. Environment Canada, Burlington, Ontario, Canada, 1–12. NWRI Cont. no. 03-171