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ADSORPTION OF DYES TO VARIOUS SIZE FRACTIONS OF SUSPENDED SOLIDS FROM THE YAMASKA RIVER, QUEBEC by

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MANAGEMENT PERSPECTIVE

The main factor governing the adsorption 0f lipophilic contaminants to suspended solids is undoubtedly organic carbon However, particle size distribution may also influence content. contaminant-suspended solids interactions, and may be relatively more important with more water-soluble or ionic contaminants which might tend to adsorb more to the clay fraction of suspended solids. In such cases, a real considerations may be more important. This article is the report of an investigation of suspended solids in the Yamaska River in the Eastern Townships of Quebec - their size distribution, and bacterial content, and the partitioning of two chemical water-soluble dyestuffs between the dissolved phase and different size fractions of suspended solids. The water-soluble dyes Acid Orange 60 and Basic Violet 1 were chosen since they are used in the Eastern Townships of Quebec, the heart of Canada's textile industry (Maguire 1989), and are representative of major use classes.

Suspended solids from the Yamaska River in Quebec have been separated into several size fractions from 3 to > 88 um, and the size fractions have been analyzed for their bacterial content as well as their ability to adsorb two water-soluble dyes. The results indicate that the suspended solids are capable of adsorbing and thus transporting significant quantities of these dyes in river water.

PERSPECTIVE-GESTION

Le principal facteur qui gouverne l'adsorption de contaminants lipophiles à des matières solides en suspension est sans aucun doute teneur en carbone organique. 1a Cependant. la distribution granulométrique peut également influencer les interactions entre contaminants et matières solides en suspension, et peut gagner relativement en importance s'il s'agit de contaminants ioniques ou davantage hydrosolubles qui peuvent tendre à être davantage adsorbés sur la fraction argileuse des matières en suspension. Cet article rapporte les résultats d'un examen des matières en suspension qui sont trouvées dans la rivière Yamaska, dans les Cantons de l'Est au Québec; l'examen portait sur la distribution granulométrique, la teneur en bactéries en produits chimiques et les populations bactériennes ainsi que sur le partage des deux colorants hydrosolubles entre la phase dissoute et les différentes fractions granulométriques des matières en Les colorants hydrosolubles Orange acide 60 et Violet suspension. alcalin 1 ont été choisis puisqu'ils sont utilisés dans les Cantons de l'Est, au coeur de l'industrie du textile au Canada (Maguire, 1989), et qu'ils sont représentatifs des principales classes de colorants utilisées.

Les matières en suspension de la Yamaska ont été partagées en différentes fractions granulométriques comprises entre 3 et plus de 88 um; les chercheurs ont dénombré les populations bactériennes ainsi que la capacité d'adsorber les deux types de colorants de chacune des fractions. Les résultats indiquent que les matières en suspension ont la capacité d'adsorber, donc de transporter, ces colorants en quantités importantes dans l'eau de la rivière.

ABSTRACT

Suspended solids from the Yamaska River in Quebec have been separated into several fractions from 3 to > 88 um, and the size fractions have been analyzed for their bacterial content as well as their ability to adsorb two water-soluble dyes. The results indicate that the suspended solids are capable of adsorbing and thus transporting significant quantities of these dyes in river water. RÉSUMÉ

Les matières en suspension de la rivière Yamaska au Québec ont été partagées en plusieurs fractions granulométriques de 3 à plus de 88 um; chaque fraction a été soumise à des analyses visant à établir la numération bactérienne et à déterminer la capacité d'adsorption de deux colorants hydrosolubles. Les résultats indiquent que les matières en suspension ont la capacité d'adsorber, donc de transporter, ces colorants en quantités importantes dans l'eau de la rivière.

INTRODUCTION

An important process in the transport and fate of lipophilic chemicals in natural water is partitioning between the operationally defined "dissolved" phase and reservoirs of organic carbon found in "compartments" such as suspended solids, sediments and biota (e.g., Karickoff, 1981). Lipophilic chemicals are frequently found in these compartments at concentrations orders of magnitude higher than in the "dissolved" phase. The suspended solids are usually defined as those that are retained by a 0.45 um filter, or by continuous flow centrifuge, and the filtrate or centrifugate is designated as the "dissolved" phase. The "dissolved" phase has been assumed to contain both truly dissolved chemicals and chemicals adsorbed to colloidal material too small to be retained by a filter or centrifuge. A model of the distribution of lipophilic chemicals in natural waters has been proposed which includes the "compartments": truly dissolved, adsorbed to suspended solids, and adsorbed to non-settling particulates or macromolecules (Gschwend and Wu, 1985). A subsequent study of the distribution of PCB congeners in Lake Superior water indicated that colloid-associated contaminants may be the dominant fraction in most surface waters, from the viewpoint of mass balance (Baker et al., 1986). This work supported an earlier contention that for lipophilic contaminants in the Great Lakes, even for compounds having sediment/ water partition coefficients of 10⁵ (K_p - (ug/g sediment)/(ug/g water), more than 90% of the water burden might exist in the dissolved fraction (Eisenreich et al., 1981). This is likely to be true for all

but the most highly lipophilic chemicals (<u>i.e.</u>, log K_{OW} > 6) in all but the most eutrophic aquatic ecosystems. If recent observations of lipophilic contaminants in basic extracts of filtered Niagara River water after prior extraction at low pH are of general significance (Maguire and Tkacz, 1989), the "dissolved" fraction may be even more important than is currently believed. Despite the foregoing observations, in water quality monitoring programs suspended solids samples are frequently taken by centrifuging large volumes of water in an effort to determine the presence of lipophilic chemicals. Although there are some limitations to this practice, it is superior to analyzing only small volumes of whole water, in which contaminants may be below limits of detection.

The main governing factor the adsorption Of lipophilic contaminants to suspended solids is undoubtedly organic carbon content (Karickhoff, 1981). However, particle size distribution may also influence contaminant-suspended solids interactions, and may be relatively more important with more water-soluble or ionic contaminants which might tend to adsorb more to the clay fraction of suspended solids. In such cases, areal considerations may be more This article is the report of an investigation of important. suspended solids in the Yamaska River in the Eastern Townships of Quebec - thie size distribution, chemical and bacterial content, and the partitioning of two water-soluble dyestuffs between the dissolved phase and different size fractions of suspended solids. The watersoluble dyes Acid Orange 60 and Basic Violet 1 were chosen since they are used in the Eastern Townships of Quebec, the heart of Canada's textile industry (Maguire, 1989), and are representative of major use classes.

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EXPERIMENTAL SECTION

Sampling Site

The Yamaska River (cf. Figure 1), a tributary of the St. Lawrence River approximately 70 km east of Montreal, has been highly polluted in the past and water quality in the basin has been generally lowe because of industrial dishcarges and inadequate waste treatment facilities (Tate, 1972; Dutka <u>et al</u>., 1988). Water samples of 200 L volume were collectged from site 5 (1 km downstream of Granby) in June and Auguest 1988. In order to minimize agitation of the water sample during transport to the laboratory, with possible disintegrtation of suspended solids, the 200 L container was filled to capacity. The water temperature was approximately 20 °C. Three days elapsed between the time the water was collected and the time of particle size analysis. Dye-binding experiments were conducted within 24 hours of fractionation.

Particle Size Distribution Analysis

The size distribution of the suspended sediment in the range 1-100 um was determined by laser particle-size analysis with a Malvern Series 2600 laser diffraction particle sizer (Bale and Morris, 1987). The particle size distribution of the samples was derived from measurements of the near-forward Fraunhofer diffraction spectrum that is provided by a particle group randomly distributed in a sample cell. Laboratory studies using dispersed particles from another source have shown that there was no appreciable difference in the grain size distribution determined by cascade filtration :(\underline{e} . \underline{q} ., Munawar \underline{et} \underline{al} ., 1983, Rao and Kwan, 1989) and the Malvern laser technique over the range 8-60 um (Droppo, personal communication, 1989). Because the material from the Yamaska River was flocculated, it was assumed that flocculated aggregates were physically stable between the time of collection and the time of analysis. This assumption appears to be valid as shown by microscopic observations of floc stability under conditions of moderate agitation of floc material on a microscopic slide (Droppo, personal communication, 1989).

Size Fractionation of Suspended Solids

A 5 L subsample of the river water was filtered using a modified cascade size fractionation procedure (Rao and Kwan, 1989) using 80, 64, 40, 20, 8 and 3 um filters (the 8&3 um filters was were polycarbonate). Extreme case was taken to minimize particle disinteggration and filter clogging by gentle mixing of the sample during filtration and gentle resuspension of the material on each sieve surface by dipping the sieve surface below the surface of the filtrate. Each of the fractions from each sieve filter was carefully resuspended in 200 mL distilled water and analyzed for bacterial content, organic carbon and nitrogen content.

Bacterial Content

A 1mL subsample of each of the fractions was diluted to 10 mL with sterile low-response water and homogenized using a vortex mixer at highest speed for 1 min. to facilitate uniform dispersal of bacteria from the particle aggregates (Marxsen, 1988). Bacterial content was then determined using the acridine orange direct microscopic counting procedure with a phase contrast microscope (Rao et al., 1984).

Organic Carbon and Nitrogen

Particulate organic carbon and nitrogen analyses were performed according to standard methods (Water Quality Branch, 1979).

Sorption of Water-Soluble Dyes

The dyes Acid Orange 60 and Basic Violet 1 were supplied by the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry, Washington, DC, USA. Their structures are given in Figures 2 and 3, and their octanol-water partition coefficients (determined by standard methods in this study) are given in Table 1.

Each 200 mL suspension of the suspended solids fractions was gently shaken with 5 ppm solutions of either dye. The concentrations of the dyes in the "dissolved" phase were determined spectrophotometrically at 24 h intervals, after the mixtures were centrifuged at 500 x g for 10 min. Monitoring wavelengths were 586 nm for Basic Violet 1 and 273 nm for Acid Orange 60. The sorption experiments were performed in the dark to exclude photodegradation. Controls were employed as a check on chemical degradation and adsorption to container walls.

RESULTS AND DISCUSSION

Table 2 shows the particle size distribution analysis and associated organic carbon and nitrogen contents of the different size fractions of particles from the Yamaska River. The figures are averages for the two samples. The 20-40 um fraction accounted for 28% of all particulates, more than any other fraction, and it had higher bacterial densities and organic carbon and nitrogen contents than other fractions. To our knowledge this is the first report of the association of bacterial populations with different particle sizes of suspended solids.

Figure 4 shows the rate of adsorption of Acid Orange 60 and Basic Violet 1 to five size fractions of suspended solids. With Acid Orange 60, apparent equilibrium was reached in approximately 48 hours with concentrations in the range 5-45 ug Acid Orange 60/mg suspended solids dry weight. Acid Orange 60 was bound with decreasing strength in the size fraction series (20-40) > (40-60) > (8-20) > (64-88) > (>88um). The logarithm of the apparent partition coefficient for this dye between the "dissolved" phase and the five size fractions test (ug

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dye/L solution/ug/dye/kg suspended solids dry weight varied from 3.6 to 4.1 at 24 - 96 hours. It was estimated that under the conditions of the experiment about 20 - 30% of the dye was bound to particulate material > 8 um.

With Basic Violet 1 equilibrium was not reached even after 96 hours, at which time dye concentrations in the suspended solids were in the range 2-12 ug Basic Violet 1/mg suspended solids dry weight. At 96 hours the concentration of Basic Violet 1 as a function of size fraction declined in the series (40-60) > (8-20) > (20-40) > (>88) > (64-88 um). It was estimated that under the conditions of the experiment of 96 hours 5-10% of the dye was bound to particulate material > 8 um. This fraction would be expected to be larger at equilibrium.

The results of this work indicate that particulate material in the Yamaska River is capable of adsorbing and transporting these two water-soluble dyestuffs. Different size fractions of the suspended solids exhibited widely varying affinities for the two dyes. This study has also shown different bacterial concentrations in different size fractions of suspended solids. Although the dyes may be adsorbed to the bacteria, earlier studies have suggested that the bacterial population does not contribute significantly to the total amount of sorption because of the low proportion of bacteria to other material such as clays, detritus and humic substances in both suspended and bottom sediments (Smith <u>et al.</u>, 1977). However, there is still the potential for bacterial transformation of dyes on suspended solids.

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REFERENCE

- Baker, J.E., Caple, P.D., and Eizenreich, S.J., (1986). Influence of colloids on sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters. Environ. Sci. Technol. <u>20</u>, 1136-1143.
- Bale, A.J., and Morris, A.W., (1987). In situ measurement of particle size in estuarine waters. Estur. Coastal Shelf Sci. <u>24</u>, 253-263.
- Dutka, B.J., Kwan, K.K., and Rao, S.S. (July 1989(. An ecotoxicological microbiological study of the Yamaska River. National Water Research Institute Report, 89-147.
- Eisenreich, S.J., Looney, B.B., and Thornton, J.D., (1981). Airborne contaminants in the Great Lakes Ecosystem. Environ. Sci. Technol. <u>15</u>, 30-38.
- Gschwend, P.M., and Wu, S., (1985). On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. Environ. Sci. Technol. <u>19</u>, 90-96.
- Karickhoff, S.W., (1981). Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemospere <u>10</u>, 833-846.

- Maguire, R.J., (March 1989). Spectral characterization of some dyestuffs used in the Eastern Townships of Quebec. National Water Research Institute Report 89-77, 88 pp.
- Maguire, R.J., and Tkacz, R.J., (1989). Potential underestimation of chlorinated hydrocarbon concentrations in fresh water. Chemosphere, in press.
- Marxsen, J., (1988). Evaluation of the importance of bacteria in the carbon flow of a small open grassland stream, the Breitenbach. Arch. Hydrobiol. <u>11</u>, 339-350.
- Munawar, M., Mudroch, A., Munawar, I.F., and Thomas, R.L., (1983). The impact of sediment-associated contaminants from the Niagara River mouth on various size assemblages of phytoplankton. J. Great Lakes Res. <u>9</u>, 303-313.
- Rao, S.S., Jorkovic, A.A., and Dutka, B.J., (1984). Some factors influencing the enumeration of metabolizing aquatic bacteria. J. Test. Eval. Amer. Soc. Test. Mater. <u>12</u>, 56-59.
- Rao, S.S., and Kwan, K.K., (1989). Methods for measuring toxicity of suspended particulates in waters. Toxicity Assess., in press.
- Smith, J.R., Mabey, W.r., Bohonos, N., Holt, B.R., Lee, S.S., Chou, T.-W., Bomberger, D.C., and Mill, T., (October 1977). Environmental pathways of selected chemicals in freshwater systems. Part I: Background and experimental procedures. US Environmental Protection Agency Report EPA-600/7-77-113, 80 pp.

- Tate, D.M., (1972). Economic and financial aspects of wastewater treatment in the Yamaska River basin, Quebec. Social Sciences Series Repaort No. 3, Inland Waters Directorate, Environment Canada, Ottawa, Ontario K1A 0E7, Canada.
- Water Quality Branch, Analytical Methods Manual. (1979). Inland Waters Directorate, Environment Canada, Ottawa, Ontario K1A 0E7, Canada.

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	Acid Orange 60	Basic Violet 1	
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Chemical Abstracts Service No.	30112-70-0	8004-87-3	
Colour Index No.	18732	42535	
Chemical Formula	C32H30N1006S2Cu	C24H28N3C1	
Molecular Weight	778.33	393.96	
Log Octanol-Water	· · · ·	r 	
Partition Coefficient	0.66+/-0.24	-(0.17 +/- 0.05)	

Table 1. Chemical Data for Acid Orange 60 and Basic Violet 1.

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Particle	% Volume	Bacterial	Particulate	Particulate
Size			Organic	Organic
Range *	in River	Densities	Carbon	Nitrogen
(mm)	Water	x10 ⁻⁵ /m1	mg/L	mg/L
			· · · · · · · · · · · · · · · · · · ·	- <u></u>
3-8	18.5+/-6.1	3.5	no data	no data
8-20	20.2+/-1.7	3.7	5.06	0.39
20-40	28.4+/-1.5	8.3	7.74	0.68
40-64	13.7+/-2.7	6.8	1.61	0.10
64-88	6.7+/3.2	3.6	0.75	0.04
>88	5.7+/-2.4	no data	3.17	>0.002

Table 2.Particle Sizes and Concentrations of Bacteria, ParticulateOrganic Carbon and Nitrogen in Yamaska River Water

* Measured by Malvern Particle Size Analyzer

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FIGURE CAPTIONS

Figure 1: Yamaska River basin in Quebec.

Figure 2: Structure of Acid Orange 60.

Figure 3: Structure of Basic Violet 1.

Figure 4. Rate of adsorption of Acid Orange 60 and Basic Violet 1 to different size fractions of suspended solids from the Yamaska River.





Fig. 2. Structure of Acid Orange 60





