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Distribution of Heavy Metals in Sediments of the Detroit River

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ABSTRACT. *The spatial distribution of 17 metals in the sediments of the Detroit River was established using metal concentrations from a river-wide survey. The survey (1999) was based on a stratified random sampling design that divided the river into upper, middle, and lower reaches and subsequently into U.S. and Canadian sides of the river. Results based on strong extraction, using concentrated acids, revealed that the Lowest Effect Level (LEL) for As, Cd, Cu, and Hg was exceeded at more than 75% of sampling sites and the Severe Effect Level (SEL) for As at 16.2% of sites. Most of the metals were homogenously distributed throughout reaches of the river, although sites with elevated concentrations were localized mainly along the middle and lower reaches as a result of a pattern of contamination sources and geographic complexity of the river, especially a spatial/temporal variability in water flow. A comparison of the results of a strong to a weak extraction (cold 5% acetic acid, to assess metal bioavailability) revealed two groups of sediment type. The first group with a "high" weak/strong ratio (bioavailable metals; about 1 for Ca, Mg, Na and from 0.6 to 0.4 for the rest of metals) was observed at sites with low flow velocities below 0.4 m s^{-1}. The "low" ratio (non-bioavailable metals; 0.25 for Ca, Mg, Na and from 0.15 to 0.05 for other metals) was observed at sites with flow velocities greater than 0.6 m s^{-1}. The data indicate that the sediment conditions, dependent on flow distribution, regulate not only the distribution of heavy metals but also can regulate metal bioavailability.*

INDEX WORDS: *Metals, contaminated sediments, strong and weak extraction, Area of Concern.*

INTRODUCTION

The Detroit River is a vector for loadings originating from the upstream lakes and connecting channels and a primary source of contaminants to Lake Erie (Kelly *et al.* 1991, Carter and Hites 1992, Koslowski *et al.* 1994, Painter *et al.* 2001, Marvin *et al*. 2002). As a source of contaminants, the influence of the river is such that contaminant concentration gradients have been observed in the western basin (Stevens and Nielson 1989, Wesloh *et al.*1992), and along the length of the river (Platford *et al.* 1985, Leadley *et al.* 1998, Lovett-Doust *et al.* 1997, Metcalfe *et al.* 2000). Although contaminant concentration gradients have been reported, there have been few studies resolving the relative importance of current and historic contaminant loadings over the entire river (Hamdy and Post 1985, Farara and Burt 1993). This lack of information has been further compounded by a failure to integrate past monitoring and research programs in a manner that would yield information as to the overall quality of the river. Previous studies on sediments of the Detroit River have been primarily limited to areas of known or suspected degradation (Zarull *et al.* 2001) and do not represent the overall health of the river ecosystem. The common approach of just sampling "problem areas" has resulted in a historically large but very biased data set representing contaminated sediments in the river (Thornley and Hamdy 1984). Furthermore, both water and sediment quality studies have been implemented in a sporadic manner, thus there are limited data sets available to quantify

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either temporal or spatial changes in the environmental quality of the system.

In 1987, the Detroit River was designated an Area of Concern (AOC) under the Great Lakes Water Quality Agreement (GLWQA) (IJC 1987). Significant environmental problems in AOCs, referred to as impaired beneficial uses, require the two federal governments develop and implement Remedial Action Plans (RAPs) in conjunction with diverse sectors (e.g., government, industry, nongovernmental organizations). Although contaminated sediment is not designated as a specific impairment in the AOCs, it is recognized as a major cause of environmental problems as well as a key factor in restoring 11 of the 14 potential impairments under the GLWQA (Zarull *et al.* 2001). Since the Upper Great Lakes Connecting Channel Study (UGLCCS 1988), significant clean up efforts have been made under RAPs (Zarull *et al*. 2001), and considerable work has been undertaken to identify the extent and severity of sediment contamination in the Detroit River. Sediments have been reported as a major source of contamination to the Detroit River water and as a factor determining contaminant levels in biota (DRCCC 1999). During the implementation of the RAP for the river, it was discovered that historic data were not sufficient to quantify either loading to the river or the overall quality of the river. Although the Detroit River can boast one of the longest records of environmental quality monitoring in the Great Lakes, simple questions as to the state of the river and whether the river was improving could not be answered (DRCCC 2002).

In order to develop a baseline on the sediment quality in the Detroit River, a river-wide sediment monitoring program was implemented in 1999. The aim of the study was to establish a benchmark for the relative importance of heavy metal pollution within the river. The sampling strategy was designed to determine the relative importance of upstream inputs associated with sediment transport and sedimentation processes in the river to local inputs along the Canadian and United States shorelines that would need to be addressed during the remedial action process. To estimate a worst-case of metal contamination, total metal concentrations were determined (total recoverable fraction). To assess a bioavailable fraction, metals were also extracted using a weak digestion protocol (Peijnenburg and Jager 2003).

METHODS

Sampling Design and Sample Collection

Sampling stations were selected according to a stratified random design in order to provide a representative description of sediment quality of the system. Stations were assigned to three reaches of the river representative of the head waters, mid section, and the lower outflow area. Sampling stations were evenly divided between the United States and Canadian portions of the river. The upper and middle reaches each contained 30 stations, while the lower reach had 90 stations. Because dredged navigation channels are less susceptible to sediment accumulation, shipping channels were de-emphasized in sampling strategy such that two-thirds of the stations were less than the median depth of the river within each respective reach. To reduce clustering of the sampling stations randomly situated within each of the reaches, the minimum allowable distance between stations was 300 m (Fig. 1).

Sampling stations were located by differential global positioning system (GPS) to ensure consistency with predetermined coordinates. Sediments were collected using a Ponar grab sampler. As sediment characteristics varied from site to site, the number of Ponar grabs required at each site varied. To standardize this spatial complexity, sampling continued at each site until 2 L of sediment was collected.

Laboratory Analyses

At the laboratory, the sediments were thoroughly mixed to ensure homogeneity and split for grain size and trace metals analyses. Sediments designated for trace metals were sieved using a 2 mm standard sieve in order to remove major detritus and animals. The < 2 mm subfraction was frozen until submitted for analysis.

The grain size distribution was performed using a method that involves passing the dried sediment through a series of graded sieves. Prior to analyses, the sediment samples were thawed, dried overnight at 110°C and mechanically disintegrated while not altering the grain size. The dried and weighed sediment subsamples (100–300 g) were transferred to the stacked column of sieves (4, 2, 1, 0.5, 0.25, 0.150, and 0.075 mm) and sieved in an automatic sieve shaker (CSC Scientific, USA) for a period 3–5 minutes. Each fraction was weighed and the results recorded.

Total recoverable mercury analysis was per-