TRACING THE CONTAMINANT HISTORY OF AN URBAN WATERSHED THROUGH AN EXAMINATION OF AQUATIC SEDIMENTS

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Abstract

The results of recent lake core, streambed, and street sediment contaminant studies, in conjunction with benchmarks studies performed in the early 1970's in the Brunette River watershed, provide a record of change which corresponds to an intense period of urbanization. Many of the contaminants currently found in the surface sediments of the watershed are above biological effects-based criteria. Pb is the trace metal of greatest concern, while Cu, Zn, Cd, Ni, Cr, and Hg levels often exceed criteria indicating possible adverse effects. A smaller organic contaminant database indicates sediment PAH levels exceed probable effect level criteria while PCB levels exceed threshold effects level criteria in a small area of the watershed. DDT and PCB levels have decreased dramatically from peak levels observed during the 1950's and 1980's, respectively, as a result of land use changes and restrictions on the use of these compounds. The recent substitution of the octane-enhancing gasoline additive MMT, replacing tetra ethyl lead, may also be responsible for decreases in Pb levels and corresponding increases in sediment Mn levels. Land activity and cover permeability have changed little in the past 20 years, however traffic density has increased by over 40% in the same time period. Analysis of traffic distribution and spatial contaminant patterns suggest traffic is a major source of Pb and Zn contamination within this watershed. Further study is required to identify the cause of recent increases in stream sediment Hg levels.

Résumé

Les résultats d'études récentes des contaminants dans les sédiments de carottes lacustres, de lits de cours d'eau et prélevés dans des rues et les résultats d'études de référence réalisées au début des années 70 dans le bassin de la Brunette montrent qu'il y a eu des changements liés à une urbanisation intense. Les concentrations de bon nombre des contaminants actuellement présents dans les sédiments de surface du bassin sont supérieures aux concentrations seuils à partir desquelles on note des effets biologiques. Le Pb est le métal trace le plus préoccupant, tandis que

Le Cu, le Zn, le Cd, le Ni, le Cr et le Hg sont présents à des concentrations souvent supérieures à celles qui peuvent entraîner des effets néfastes. Une plus petite base de données sur les contaminants organiques montre que les niveaux de HAP dans les sédiments excèdent les niveaux pouvant entraîner des effets néfastes, tandis que les niveaux de PCB excèdent le niveau seuil d'effets néfastes dans une petite portion du bassin. Les niveaux de DDT et de PCB ont chuté de façon marquée par rapport aux pics observés dans les années 50 et 80, respectivement, par suite de changements dans l'utilisation des terres et de l'imposition de restrictions quant à l'usage de ces composés. Le remplacement récent du plomb tétraéthyle par le MMT, un additif de la gazoline remonteur d'octane, peut aussi être responsable des diminutions des concentrations de Pb et des augmentations correspondantes des concentrations de Mn dans les sédiments. L'utilisation et la perméabilité des terres ont peu varié au cours des 20 dernières années; cependant, la densité du trafic s'est accrue de plus de 40 % durant cette période. L'analyse de la distribution du trafic et des contaminants laissent penser que le trafic est une source majeure de contamination par le Pb et le Zn dans ce bassin hydrographique. On devra mener d'autres études pour identifier la cause des accroissements récents des niveaux de Hg dans les sédiments des cours d'eau.

Table of Contents

List of Tables

1.0 Introduction

Sediments were chosen as the media of analysis in this study because of the “particle-reactive” nature of many contaminant compounds. Many contaminants entering an aquatic system quickly adsorb to sediments and eventually settle out of the water column. This interaction between contaminants and sediments potentially alters the benthic environment and also leaves, in-place, a record of contaminant history. This study has evaluated the current risk to the aquatic environment by comparing the results of contaminant levels in surface sediment samples obtained from streams throughout the watershed to recently developed interim Canadian sediment guidelines (Smith et al., 1995). These guidelines, which are biological-effects based, define a threshold effects level (TEL) which indicates the possibility of adverse biological effects, and a probable effects level (PEL) which indicates a high probability of biological effects, for most contaminants of concern in urban runoff.

The watershed contaminant history has been determined by two different approaches. The first approach compares current surface sediment contaminant concentrations with levels recorded at the same locations during a baseline study conducted in 1973 and 1974 (Hall et al., 1976). This approach clearly shows net changes in pollutant loadings over 20 years but provides no information prior to 1973 or detail of recent changes. The second approach utilizes a long Burnaby Lake sediment core -- dated using a radioisotope method (210Pb) -- to provide a contaminant history spanning the previous 150 years.

2.0 Methods

A summary of sample preparation and analytical methods is provided for each of the individual contaminant and land use studies. Full methodological details can be found in the following reference documents. Trace metal and chlorinated hydrocarbon analytical methods used in the baseline studies (1973/74) are detailed in Hall et al. (1976). Methods used in recent trace metals studies and land use analysis are outlined in McCallum (1995). The analytical methods used to measure PAH in stream and street sediments collected in 1979 are included in Morton (1983).

Sampling locations for streambed and street sediments were defined in the baseline studies. Thirty-three of the original 36 stream locations and 24 of 25 original street locations were re-sampled for trace metal analysis in 1993. Chlorinated hydrocarbon analysis was performed on samples obtained at all the 25 street locations and 26 stream locations in 1973/74. Samples from 8 (of the original 26) stream locations were analyzed for chlorinated hydrocarbon analysis in 1993. Four locations in Still Creek were sampled for PAH in 1979. A 563 cm lake core, from which sub-samples were analyzed for trace metals and chlorinated hydrocarbons, was retrieved from Burnaby Lake in 1994, using a modified Livingstone piston corer. All locations sampled in 1993/94 are shown on Fig.1.

Streambed and street sediment samples were first passed through a 177μm sieve (retaining the fine portion) prior to trace metal and chlorinated hydrocarbon analysis (1993 only). Samples for chlorinated hydrocarbon analysis in 1973/74 and for PAH analysis in 1979 were unmodified prior to extraction procedures. Lake core sub-samples were combusted at 550 C to remove organic matter prior to trace metal (ex. Hg) determinations. Analysis of chlorinated hydrocarbons and Hg in the lake core was performed on unmodified sub-samples.

The elements Fe, Mn, Cu, Zn, Pb, Ni, Co, Ag, and Cd were determined in 1973 in 2 separate extractions which utilized concentrated nitric/perchloric acid ("total" digest") and cold 0.5 N HCl acid ("extractable" digest). An atomic absorption spectrophotometer with an air-acetylene flame was used for detection. The same techniques (without perchloric acid) were used to measure Fe, Mn, Cu, Zn, Pb, Ni, and Cr in streambed and street samples obtained in 1993. Cadmium was detected using a graphite furnace atomic absorption spectrophotometer in 1993. Mercury was determined in each study using cold vapour atomic absorption spectrophotometry. An Inductively Coupled Plasma atomic emission spectrophotometer was used to detect Fe, Mn, Cu, Zn, Pb, Ni, Cd, and Cr in the Burnaby Lake core samples (digested with conc. nitric acid). The sediment core was dated by the ^{210}Pb method for the last 150 year period.

Chlorinated hydrocarbons were extracted from the sediment samples using acetone as an initial solvent and then partitioning into hexane. Individual compounds were detected using gas chromatography and electron capture detectors (GC/ECD). The method detection limits (dry

weight) for chlorinated pesticides were 1 µg/kg in 1973/74 and 2 µg/kg in 1993. Detection limits for PCB were 10 µg/kg dry weight in both studies.

Polycyclic aromatic hydrocarbons were determined by alkaline digestion of streambed and street sediment samples was followed by solvent-solvent partition and Florisil column chromatography. Preliminary separation of compounds was effected by an alumina column clean-up procedure. Final determination of compounds was achieved by using high pressure liquid chromatography (HPLC) with UV spectrophotometry detection .

Geographic Information Systems (GIS) were utilized in the analysis of land use. Digitized 1:20,000 TRIM (Terrain Resource Inventory Management) map sheets served as a base map, while land activity and land cover were digitized from aerial photos for both the 1973 and 1993 period. Traffic analysis was facilitated with the model output (for Fall, 1992) from GVRD's EMME/2 transportation model (Greater Vancouver Regional District, 1992).

3.0 Discussion of Results

3.1 Comparison to biological effects-based criteria

The most recent stream sediment contaminant results have been compared to criteria to provide a measure of risk imposed on the aquatic environment. The results of this comparison, illustrated in Fig.2, indicates probable effects level (PEL) criteria are most often exceeded in the Still Creek area of the watershed. Lead is the trace metal posing the greatest threat to aquatic health, followed by Cu, Zn, and Hg. At least one PAH compound exceeds PEL criteria at each of the 4 sites sampled in 1979. Possible effects, indicated by exceedances of threshold effects level (TEL) criteria have been recorded throughout the watershed for Pb, Cu, Zn, and at fewer locations for Hg, Cd, Ni, and Cr. Of the recent chlorinated hydrocarbon analyses, only PCB concentrations at 3 of 8 sampled locations exceeded TEL criteria.

3.2 Contaminant trends

Contaminant loading to the western portion of Burnaby Lake, measured in the lake core, is presented in Fig.3. The accompanying plot of Burnaby residential population illustrates an apparent correlation between rising contaminant levels and early population increases, with the exception of DDT degradation compounds. Decreases in the loading rates of these compounds (p,p'-DDD and p,p'-DDE), beginning around 1950, can be attributed to accelerated watershed urbanization and declining agricultural land use. Later restrictions on the sale of the pesticide in 1973 (Wong, 1996) would have accelerated the declining contaminant loads.

Declining lake core Pb and PCB contaminant loads, starting between 1970 and 1980 is the probable result of similar restrictions on commercial products. The octane-enhancing gasoline additive, tetra ethyl lead, accounted for approximately 70% of total Canadian lead emissions to the atmosphere at its peak usage in 1973 (Poon, 1989). Since that time, the additive has been gradually phased out and was completely eliminated from gasoline in 1990. Similarly, the manufacture of PCB in the United States was prohibited in 1977 and an accelerated Canadian phase-out program was initiated in 1985 (Environment Canada, 1987). Contaminant levels measured in stream and street sediments in 1973/74 and 1993 provides additional information relating to recent changes. As shown in Table 1, the levels of Pb, PCB, and DDT-related compounds have all declined in the last 20 years, confirming lake core results.

On a percentage basis, Hg levels in stream sediments have increased more than any other measured contaminant between 1973 and 1993 (Table 1). The overall increase may be over-stated, though, because the method detection limit (MDL) of the 1973 procedure is not known (instrument detection limit reported as 0.001 mg/kg), and 22 of 33 measurements recorded in 1973 were below the 1993 MDL (0.030 mg/kg). An alternative estimate of change in stream sediment Hg levels over the last 20 years can be obtained by replacing all 1973 values below the 1993 MDL with the value of 0.030 mg/kg. Using this conservative approach, the median increase between 1973 and 1993 is 140 %. This result and the 81 % median increase in Cu levels in stream sediments during the same time period contradict the declining trend observed in the lake core. Past industrial land usage, prior to implementation of waste management

regulations, may explain this apparent contradiction. Beginning with the first zoning of industrial land in the watershed in 1947, industrial expansion has concentrated largely in the Still Creek area (Dawson et al., 1985). Point source discharges from industries such as electroplating were known as significant polluters during the 1970's and efforts were made to eliminate the sources (Hall and Wiens, 1976). The recent decline of Cu and Hg recorded in the lake core may be the result of the abatement of industrial point-source pollution into Still Creek, while levels throughout the watershed are rising.

Manganese has increased markedly in stream and street sediments since 1973; an increase most dramatically observed in the "extractable" form (Table 1). The increase cannot be confirmed in lake core analyses because of the mobility of Mn ions in buried sediment. This increase in stream sediment levels corresponds, in time, to the introduction of the gasoline additive, methylcyclopentadienyl manganese tricarbonyl (MMT), as a replacement for tetra ethyl lead, in 1974. Estimated automotive emissions now rank second only to steel and alloy production, in terms of total anthropogenic Mn sources to the Canadian environment (McCallum, 1995). It is difficult to determine the aquatic health risk resulting from increased Mn levels because of the lack of Canadian sediment criteria and the large natural variability observed in sediments. Borrowing biological effects-based criteria developed in Ontario (Jaagumagi, 1992), 11 of 33 stream sediment sampling locations in the Brunette Watershed exceed the severe effects level criterion (1100 mg/kg).

3.3 Contaminant relationships to recent land use trends

Changes in general land use activities (i.e.,. residential, commercial, industrial) and permeable ground cover have been relatively small over the last 20 years (Table 2) and therefore are not likely responsible for the large changes observed in sediment trace metal levels. The relatively large increases in traffic density throughout the watershed, however, may be responsible for some of the changes in contaminant levels.

Results of the 3 independent statistical comparisons in Table 3 indicate that traffic emissions are a probable source of the watershed Pb and Zn contamination. Copper, Cr, and Ni levels are less consistently related to traffic indices. Somewhat surprisingly, the two elements which increased by the largest (relative) amounts over the last 20 years — Hg and Mn —do not exhibit a spatial correlation with traffic. A possible explanation of the Mn results is related to the unique geochemical properties of the element. Manganese, in its solid, oxidized form, can act as catalyst in the oxidation and precipitation of soluble Mn (Hem, 1981). Extrapolating Hem's laboratory results to stream conditions, solid Mn oxides emitted from cars would scavenge soluble stream Mn, thereby significantly increasing sediment levels. The large increase in "extractable" sediment Mn supports this hypothesis. The cause of the large Hg increase is not clear. Dentistry and fungicides in lawn and garden fertilizers are known sources of Hg, yet there has been no indication that either of these sources have experienced unusually large growth in the watershed over the last 20 years. A nearby municipal solid waste incinerator, in operation since 1988, is a new source of Hg to the watershed which may account for some of the increases observed in stream sediment levels.

3.4 Summary

Contamination of aquatic sediments early in this century, as recorded in lake core sediments, closely paralleled human population increases to the watershed. Changes in land use from an agricultural base to urban in the 1950s resulted in decreased concentrations of the chlorinated pesticide, DDT, and increases in urban-related contaminants such as PCB, Pb, Cu, Zn, and Hg. Both Pb and PCB levels have decreased in recent years as a probable result of the restrictions on the sale and use of tetra ethyl lead and PCB.

Lead poses the greatest known risk to aquatic health based on comparisons to biological effects-based sediment criteria. The very limited database of PAH concentrations suggest this group of compounds may also be a threat to aquatic life in the watershed and deserves further study. Recent large increases in Mn concentrations are another potential source of immediate concern in this area.

A spatial analysis of land use and trace metal levels indicates strongly that traffic is a significant source of both Pb and Zn to the watershed. At the present rate of increase, Zn levels may pose significant risks to aquatic health throughout the watershed within the next 20 years. The recent addition of a Mn-based gasoline additive (MMT) is the probable cause of very large increases in stream sediment levels. Large increases in Hg levels do not appear to be related to traffic and further study is required to determine the causes.

3.5 References

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Tables

Table 1 Changes in stream and street contaminant levels between 1973 and 1993.

Contaminant	Media (digestion[1])	Median of sampling locations (mg/kg dry)		Median difference[2] between 1973/4 and 1994
		1973/74	1993	(%)
Pb	stream (total)	79	63	- 35
	stream (extr)	57	54	- 16
	street (total)	637	222	- 67
Cu	stream (total)	38	56	81
	stream (extr)	21	31	49
	street (total)	166	129	- 43
Zn	stream (total)	109	143	45
	stream (extr)	76	75	33
	street (total)	316	373	6
Hg	stream (total)	0.022	0.098	290
	street (total)	0.038	0.045	- 4
Mn	stream (total)	320	807	131
	stream (extr)	22	492	2600
	street (total)	240	315	43
Ni	stream (total)	13	14	- 7
	stream (extr)	9	< 6	indeterminate
	street (total)	33	30	- 13
Cd	stream (total)	<0.1	0.40	indeterminate
	street (total)	1.5	0.83	- 43
PCB (1254)	stream	0.138	0.020	- 91
p,p'-DDT	stream	0.008	< 0.002	indeterminate
p,p'-DDE	stream	< 0.001	< 0.002	indeterminate
p,p'-DDD	stream	0.007	< 0.002	indeterminate

Notes:

1. "total" refers to strong acid digestion methods used in 1973 and 1993; "extr" refers to cold, weak acid (extractable) digestion method used in both studies.

2. Percentage difference between years calculated at each sampling station; number reported is the median of all calculated differences.

Table 2 Changes in Brunette Watershed land use and traffic between 1973 and 1993.

Land Use / Land cover/ Traffic	Units	1973	1993	% Change
Residential	% of total area	40.8	45.7	+ 4.9
Industrial	% of total area	11.9	13.2	+ 1.3
Commercial	% of total area	3.6	4.1	+ 0.5
Institutional	% of total area	6.6	6.4	- 0.2
Agricultural	% of total area	1.4	0	- 1.4
Permeable ground cover	% of total area	66	59	- 7.0
Traffic density	million vehicle km per day	3.0	4.3	+ 44

Table 3 **Relationships between sediment trace metal levels and traffic.**

Trace metal	Street sediment levels enriched relative to stream sediments ?[1]	Street sediment levels related to street traffic *intensity* ?[2]	Stream sediment levels related to sub-catchment traffic *density*?[3]
Pb	yes	yes	yes
Zn	yes	yes	yes
Cu	yes	no	yes
Cr	yes	yes	no
Ni	yes	no	no
Hg	no	no	no
Mn	no	no	no

Notes:

1. Metal is considered enriched if median street sediment value exceeds median stream sediment value.

2. Street sampling locations divided into 2 groups of equal size (n=12) based on street traffic volumes. If trace metal levels are significantly different between groups (Mann-Whitney U test, a = 0.10), then street sediment trace metal levels are potentially related to local traffic intensity.

3. Comparison between stream stations located in high traffic density "Still Creek" sub-catchment (n=12), and stream stations in lower (by half) traffic density "Brunette River" sub-catchment (n=13). If trace metal levels are significantly different between groups (Mann-Whitney U test, a = 0.05), then stream sediment trace metal levels are potentially related to sub-catchment traffic density.