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CHARACTERIZATION OF URBAN RUNOFF
IN SAULT STE. MARIE

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ABSTRACT

Concerns about pollution of the St. Mary's River in Sault Ste. Marie led to the selection of this area as one of the demonstration sites under the MISA program. Consequently, it was required to characterize various point and nonpoint sources of pollution, including urban runoff, in this area. Runoff characteristics are presented for 17 water quality parameters and further used to estimate annual pollutant loadings which were compared to those from point sources. It was found that the point sources predominated the total loadings of chloride, ammonia, phosphorus, zinc, mercury, oil and grease, cyanides, and phenols. Urban runoff produced comparable or predominant loadings of lead, copper, nickel, cobalt, cadmium, PAHs, PCBs, and HCB. The computed loadings are suitable for use as loading inputs in the modelling of water quality in the St. Mary's River.

RÉSUMÉ

La situation préoccupante relative à la pollution de la rivière St. Mary's à Sault-Sainte-Marie a motivé la sélection de la région comme site de démonstration du programme SMID. Il a donc été nécessaire de caractériser diverses sources ponctuelles et non ponctuelles de pollution dans la région, y compris le ruissellement urbain. Les caractéristiques du ruissellement, présentées en fonction de 17 paramètres de qualité de l'eau, servent en plus à estimer les charges annuelles de polluants qui ont été comparées à celles des sources ponctuelles. On a découvert que les sources ponctuelles dominaient dans les charges totales de chlorures, d'ammoniaque, de phosphore, de zinc, de mercure, d'huile et de matières grasses, de cyanures et de phénols. On a relevé dans le ruissellement urbain des charges comparables ou dominantes de plomb, de cuivre, de nickel, de cobalt, de cadmium, de HAP, de PCB et de HCB. Les charges calculées peuvent servir de données d'entrée en modélisation de la qualité de l'eau de la rivière St. Mary's.

MANAGEMENT PERSPECTIVE

In spite of recent improvements in control of point source pollution by technology-based effluent limitations, in many waters, the water quality goals and designated uses are unattainable without some control of nonpoint source pollution. Consequently, the abatement of nonpoint source pollution is attracting more attention as one of major control options in water quality management. In the report that follows urban runoff is evaluated as a nonpoint source of pollution and compared to urban point sources. The results and methodologies presented are applicable in comparative evaluations of pollutant sources and planning-level studies of urban nonpoint source pollution.

PERSPECTIVE - GESTION

En dépit d'améliorations récentes pour réduire, dans bon nombre de plans d'eau, les contaminants libérés par les sources ponctuelles, en limitant les effluents par des moyens technologiques, les objectifs de qualité de l'eau et leurs utilisations désignées sont irréalisables sans une certaine dépollution du milieu contaminé par les sources non ponctuelles. C'est ce qui explique l'attrait croissant de la lutte contre les sources non ponctuelles parmi les principales options de dépollution en gestion de la qualité de l'eau. Dans ce rapport, le ruissellement urbain, source de pollution non ponctuelle, est évalué et comparé aux sources ponctuelles urbaines. La méthodologie et les résultats présentés sont applicables à l'évaluation comparative des sources de pollution ainsi qu'aux études de pollution par les sources non ponctuelles urbaines, effectuées à des fins de planification.

INTRODUCTION

Under the Upper Great Lakes Connecting Channels (UGLCC) Study, various point and nonpoint sources of pollution were studied in several cities in the UGLCC area including Sault Ste. Marie. One of the sources investigated was urban runoff whose composition was characterized for selected parameters and the annual pollutant loadings conveyed by runoff were estimated. Following the completion of this study, further investigations of polynuclear aromatic hydrocarbons (PAHs) were conducted in the city during the period from 1986 to 1988. The results of all such investigations of urban runoff and some comments on bacteriological characteristics of stormwater in Sault Ste. Marie are presented in the report that follows.

CHARACTERISTICS OF URBAN RUNOFF IN SAULT STE. MARIE

Study Area

The City of Sault Ste. Marie has a population of about 82,900 inhabitants and is located along the St. Mary's River which represents the principal water body in this urban area. Principal uses of the river include navigation, power generation, water supply, wild life habitat, and transport of stormwater and wastewater effluents.

Water quality in the St. Mary's River has been of some concern, particularly the levels of polyaromatic hydrocarbons (PAH's) and some other industrial chemicals. For that reason, the river has been selected as one of the study sites under the MISA program currently conducted by the (Ontario) Ministry of the Environment.

Surface drainage in the City of Sault Ste. Marie is provided by storm sewers which discharge either directly into the St. Mary's River or into one of several creeks draining into the river. Stormwater outfalls are shown in Figure 1.

Study Approach

Urban runoff, in the form of stormwater discharges or combined sewer overflows, represents a diffuse source of pollutants intermittently discharged into the receiving waters at numerous points. Consequently, it is impossible to monitor all the discharge points and runoff events, and other approaches to estimating the pollutant loadings need to be taken.

Pollutant loadings in urban runoff can be generally estimated by one of several methods depending on the level of analysis and the size of the area.

In detailed analysis of small catchments, the best estimates of runoff loadings are obtained from field measurements (Huber, 1986), or from detailed simulations with calibrated mathematical models (Novotny _et al_., 1985). In a planning-level analysis of large areas, the loadings are calculated from empirical load functions, in the form of unit area loading rates or mean concentrations, for various types of land use (Sullivan _et_ _al_., 1978; U.S. EPA, 1983). Although the ability of general load functions to estimate loadings from specific areas may be questioned, such functions were derived from large samples of data from many catchments and this contributes to their general applicability (U.S. EPA, 1983).

Methodology for Loading Computations

The goals of the loading computation method used in this study are to retain some simplicity of the methods based on general loading rates and, at the same time, to reflect local conditions. The annual loading of pollutant j in runoff from an area with a particular land use can be expressed as

$$L_j = \sum_{i=1}^{N} Q_i C_{ji} \tag{1}$$

where subscript $i = 1,\ldots N$ denotes individual events during the year, Q_i is the event runoff volume, and C_{ji} is the event mean concentration. Eq. (1) can be further simplified by recognizing weak correlation between Q and C, as found for example in the Nationwide Urban Runoff Program (NURP) (U.S. EPA, 1983), and introducing a mean concentration C_j. Eq. (1) is then rewritten as

$$L_j = C_j V \tag{2}$$

where $V = \sum_{1}^{N} Q_i$ is the annual runoff volume, and the annual mean concentration C_j is estimated from field data as

$$C_j = \sum_{i=1}^{N} (C_{ji} Q_i)/V = \frac{1}{n} \sum_{i=1}^{n} C_{ji} \tag{3}$$

where n is the number of events actually sampled. The total loading for an urban area is then obtained by summation of contributions from individual land use types.

The annual runoff volume V can be adequately estimated by approximate methods, including the runoff coefficient method (U.S. EPA, 1983), the Soil Conservation Service method (Kibler, 1982), and the STORM model (U.S. Army Corps of Engineers, 1977). The main difficulty in application of eq. (2) is the estimation of C_j by field sampling recognizing that, in the planning-level of analysis, the target accuracy may be as low as an order of magnitude and can be achieved with a relatively small number of samples.

Field sampling should characterize three sources of variability in C_j - during individual runoff events, between events, and among sites. Variability during events can be accounted for by collecting flow-proportional composite samples.

Variability between events requires to sample a number of events at each site. Although the minimum number of events to be sampled cannot be specified a priori, it is possible to continue sampling until the uncertainties in the mean concentrations become so low that they do not affect the outcome of relative comparisons of total nonpoint and point source loadings. In the NURP Program, variability due to sampling was described by the coefficient of variation which typically attained values in the range from 0.5 to 1.0. The reported weak correlation between event runoff volumes and mean concentrations makes it acceptable to sample events of any magnitude, without a particular emphasis on large events (U.S. EPA, 1983).

Finally, to characterize variability in C among sites, it is required to sample in areas with various land use and rates of export of pollutants. Representativeness of samples is increased by establishing sampling sites with large contributing areas.

Urban Land Runoff Volumes

Estimates of the annual volumes of runoff from the study area were produced by the STORM model (U.S. Army Corps of Engineers, 1977) which was run for one year with the annual precipitation approximating the long-term average. Although the model was not calibrated, the selection of model parameters was guided by a sensitivity analysis and the literature data. In the sensitivity analysis, model input data were varied within a practical range of values (Marsalek and Ng, 1987). It was noted that among the input data, only the runoff coefficients for impervious and pervious areas had significant impacts on computed volumes. The adopted value of the runoff coefficient for impervious areas was verified against the literature data recognizing that the values of this coefficient are well established and may be transposed among various locations (Kibler, 1982). Therefore, the main source of uncertainty in runoff calculations is the runoff coefficient for pervious areas.

From the point of view of pollution generation, contributions from urban pervious areas, generally represented by grassed areas, are relatively small, because runoff from such areas is much less polluted than runoff from impervious areas (U.S. EPA, 1983). Consequently, even significant uncertainties in volumes of runoff from pervious areas may be acceptable, because of their limited impact on pollution loadings.

Stormwater discharges in Sault Ste. Marie were determined as 13.0 million m^3/yr.

Runoff Composition

The list of constituents studied, which is shown in Table 1, was established by analysis of water quality problems in the study area (UGLCC Study Workgroup, 1988). All such constituents were deemed important for design of remedial measures.

The study resources, in terms of personnel, field equipment and analytical support, allowed the establishment of three sites for regular sampling of stormwater. These sites, shown in Figure 1, were distributed among residential, commercial and industrial areas. Additional sites, which were established for investigations of polynuclear aromatic hydrocarbons (PAHs), are described later. Considering the relatively low accuracy required and the observed limited variability of runoff composition among sites, the total number of sampling sites was found adequate.

Stormwater samples were collected by means of sewer inlet samplers which collect directly flow-proportional samples (Marsalek and Ng, 1987). This type of sampling does not reflect temporary variations in water quality caused by storage in catch basins or sewers, which were considered unimportant over extended time periods. However, another limitation of sampling at sewer inlets should be recognized - it cannot detect illicit discharges from point sources into storm sewers (Schmidt and Spencer, 1986). Such discharges were not considered important in the nonindustrial parts of the study area, and in industrial parts, some storm drains with possible contamination from point sources were considered as point sources (UGLCC Study Workgroup, 1988).

RESULTS

Sampling results were used to estimate mean pollutant concentrations for residential, commercial and industrial land. Using such mean concentrations and the corresponding annual runoff volumes, the pollutant subloadings were computed for individual land use types and then summed up to yield the total loadings for all individual constituents except chloride (Marsalek and Ng, 1987). Chloride originates from winter road salting and its concentrations in urban runoff vary so much during the year that it was not feasible to characterize them by limited sampling. Consequently, the chloride loadings were estimated from road salt usage records assuming, somewhat conservatively, that all salt is washed off by runoff.

The mean concentrations of pollutants in stormwater from the study area can be determined by division of the total loadings by the total annual runoff volume. Such concentrations are shown in Table 2 together with some literature data (Marsalek and Schroeter, 1984; U.S. EPA, 1983) and the hypothetical equivalent point source concentrations, which were defined as the annual point source loadings divided by the annual volume of stormwater. The data in Table 2 can serve for verification of runoff characteristics against the literature data and a quick evaluation of stormwater pollutant levels. The stormwater loadings are comparable to the point source loadings if the pollutant levels in runoff are comparable to the equivalent point-source levels shown in Table 2.

Finally, the stormwater loadings were added to the point source loadings determined by the UGLCC Study Workshop Workgroup (1988) to obtain the total loadings from all sources and the relative contributions of various nonpoint and point sources. The distributions of total loadings among individual sources are presented in Figure 2.

DISCUSSION OF RESULTS

Discussion of results focuses on uncertainties in loading estimates, verification of stormwater composition data, comparison of sources, and a general evaluation of the methodology used.

Uncertainties in the nonpoint source loadings should be considered in the context of the primary use of such data for comparisons of relative contributions of pollutant sources and development of cost effective remedial measures. For the majority of constituents studied, the total loadings are clearly dominated by point sources and even considerable uncertainties in nonpoint loadings may be acceptable as long as they do not affect water management decisions.

Variations in mean concentrations in stormwater from individual cities are small for relatively common pollutants (Marsalek and Ng, 1987). Consequently, a limited number of sampling sites is sufficient to obtain runoff characterization for these pollutants. Larger differences become apparent for less common substances, such as HCB, PAHs and PCBs, which originate from local industrial sources, and more extensive sampling may be required for such substances.

For nine constituents listed in Table 1, the concentration data from the study area were compared to similar data, based on event mean concentrations, representing a wide range of urban areas (Marsalek and Schroeter, 1984; U.S. EPA, 1983). A good agreement was found for five fairly common constituents, total phosphorus, copper, lead, zinc, and nickel. For these constituents, the use of the literature data would have produced loadings fully comparable to those obtained from field sampling. For the remaining four constituents, the agreement for cobalt, PCBs and cadmium was fair, and poor for HCB. It appears from these comparisons that the general data bases provided fairly reliable results for substances commonly occurring in urban areas, but their usefulness was reduced for less common substances occurring at very low levels and originating from local industrial sources.

The initial experimental design of the sampling network was based on assumed significance of land use effects on runoff quality. Such a concept had been first proposed in the early studies of stormwater composition and later adopted in many urban runoff models (Huber, 1986). Recent findings indicate that land use, described by general categories, does not offer a reliable basis for explaining differences in runoff composition at various sites (U.S. EPA, 1983). This follows from the fact that even though land use affects fluxes of pollutants produced at the site, it has a minimal impact on imports of pollutants from other areas. Furthermore, general land use categories do not adequately describe the frequency and intensity of activities leading to production of pollutants.

In planning-level analysis, it was of interest to test the feasibility of combining runoff quality data for various land use into a single data set and using its mean in loading computations. This simplified method produced loadings which were fully comparable to those obtained by summation of loadings for individual land use types and presented in Table 2. A perfect agreement would be obtained by defining the city-wide mean concentrations as weighted means of land-use concentrations, where the weighting factor would be the relative contributions of areas with specific land use to the total volume of runoff.

The comparisons of point and nonpoint source loadings indicate that for majority of parameters, the point source loadings predominate the total loadings. Considering the distribution plots in Figure 2, out of 17 cases, the point sources predominated in about one half of all cases, the nonpoint sources in 25%, and the remaining 25% were comparable. The predomination of point sources was particularly strong for ammonia, phosphorus, iron, phenols, cyanide, oil and grease, and mercury. The nonpoint sources predominated the relatively low loadings of copper, cadmium, PCBs, and HCB. The results of these comparisons were not affected by uncertainties in nonpoint loadings which were discussed earlier.

The source loading comparisons and particularly the equivalent point source concentrations in Table 2 further suggest that the evaluations of point sources, which are straight forward, should be done before those of nonpoint sources. Examination of point source loadings and their equivalent concentrations would reduce the list of constituents that need to be evaluated for nonpoint sources. For example, the point source equivalent concentrations of ammonia, phosphorus, zinc, cyanides, phenols, and oil and grease in Table 2 are so high that no field sampling of nonpoint sources would be required to reach conclusions that the loadings of these constituents are fully predominated by point sources.

Comparisons against the general data bases indicate that the proposed methodology for evaluation of urban runoff loadings is fairly effective and its main use would be for less common constituents which either are not included in general data bases or are so rare that mean concentrations from data bases have a limited validity.

If the planning-level analysis of nonpoint sources yields loadings comparable to those from point sources, further, more detailed investigations of nonpoint sources may be warranted. Such investigations should be limited to critical pollutants with comparable loadings and their main purpose would be to reduce uncertainties in estimates of nonpoint loadings.

STUDIES OF PAHs

The data on PAHs in urban runoff from Sault Ste. Marie, collected under the UGLCC study, very fairly limited in terms of the substances studied and scope of the sampling program. In view of the strong interest in PAHs loadings in the St. Mary's River area and recognizing the limitations of the earlier collected data, it was decided to continue the investigations of PAHs in runoff from the study area. This study extension was done in two stages, firstly by investigating aerial depositions of PAHs in urban snowpack and, secondly, by subsequent sampling of various runoff sources in the study area. The results of these investigations are presented in the chronological order.

Investigations of PAHs in the Snowpack

Urban snowpack functions as an effective trap of depositions of various conservative pollutants, including PAHs. It is therefore feasible to use the accumulated rates for estimating the deposition rates, as done in this study. Details of such investigations, which were presented by Boom and Marsalek (1988), are briefly summarized below.

Parameters Studied

The selection of the PAH substances to be studied was restricted by the available analytical support to the 17 PAH substances listed in Table 1. This list includes perhaps the most extensively studied and highly carcinogenic PAH substance, benzo[a]pyrene, the remaining five PAHs in the Borneff group, fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene;

and 12 of the 17 PAHs included on the EPA list of priority pollutants. Table 1 also shows the detection limits of the employed analytical procedures.

Sampling Sites and Procedures

In the study area, 20 sampling stations were selected in a grid centred around the steel plant property. The sampling grid points were spaced from 1.2 to 16 km from the centre. The greatest density of sites followed the east-west direction, which was the direction of the predominant winds during the sampling period. The sampling stations had to be accessible, somewhat remote from the major traffic routes, and had to possess an undisturbed snowpack representing average conditions in the local area. Ideal sites were found in parks, open land areas and backyards. Snowpack samples were collected by a stainless steel core sampler with a cross-section of 0.15 x 0.15 m.

PAH Concentrations and Frequencies of Detection

Analysis of the unfiltered melt-water samples yielded concentrations of individual PAH substances in the snowpack at the end of the snow accumulation period of almost 11 weeks. The observed concentrations are listed in Table 3.

PAH concentration data in Table 3 show great variations, ranging from values below the detection limit to ~7 µg/L. The frequency of detection varied among the substances studied from zero to 90%. The three undetected substances, indene, 1,2,3,4-tetrahydronaphthalene and 2-chloronaphthalene, are of limited interest and, consequently, they were omitted from further analysis. Phenanthrene, fluoranthene and pyrene were detected in 90% of all samples. Their levels dropped below the detection limit only at remote stations in rural areas serving as background stations. The most carcinogenic substance studied, benzo[α]pyrene, was detected in 30% of all samples. In general, the frequency of detection depended not only on the type of substance, but also on the sampling location. With regard to the location, both the distance from the grid centre and the direction were important. The highest concentrations were detected for fairly common substances, such as fluoranthene, phenanthrene and pyrene. Their concentrations were generally in the order of 1 µg/L. The very carcinogenic benzo[α]pyrene was detected at levels of one order of magnitude lower.

PAH Loading Rates in the Snowpack

The concentration data were used to calculate loading rates of PAHs stored in the snowpack. Such rates were calculated as $m = CV/A$, where m is the loading rate (µg m^{-2}), C is the concentration (µg/L), V is the volume of melt-water (L), and A is the snowpack area sampled

(m^2). The calculated loading rates were approximated by isoloading contours shown in Figure 3.

The loading rates in Figure 3 correspond to an accumulation period of 11 weeks and range from 90 to 1600 $\mu g\ m^{-2}$. In calculations of these loading rates, the data below the detection limit were simply set equal to one half of the limit. This expedient somewhat increased the uncertainty in the reported data, but not significantly. The uncertainties caused by the above treatment of data below detection were described by their weighted average of 11%, when using the loading rate as a weighting factor.

The isoloading contours in Figure 3 generally follow the outline of the urban area studied, except for the obvious elongation in the westerly direction. In the northerly and easterly directions, the areal loadings drop off very quickly below the detection limits but, in the westerly direction, the contours extend well outside of the city. This observation implies air transport of PAHs from urban sources and such transport should be related to the distribution of wind directions during the period of PAHs accumulation. To verify this hypothesis, hourly wind directions recorded during the accumulation period were analyzed. After neglecting some minor snowfall early in the season, the accumulation period was taken from November 15, 1986 to February 24, 1987. The frequency distribution of wind direction for that period is shown in Figure 3 and clearly shows the predominance of easterly winds responsible for the displacement of the loading contours in the westerly direction.

The isoloading contours can be used to estimate the total quantity of PAHs stored in the snowpack in the study area. For this purpose, the areas between the loading contours were integrated and, using the mean loading rates, the total loading of the PAHs studied was calculated as ~18 kg. The uncertainty in this estimate caused by the data below the detection limit was relatively low, ~10%. A similar calculation for the Borneff group of six PAHs produced their loading in the snowpack as 8 kg.

The PAH accumulations in the snowpack could also be used to estimate annual depositions. Although the data on hand refer to winter conditions, Seifert and Lahmann (1980) showed that, in industrial urban areas, there are no seasonal variations in PAH depositions. Using this assumption, the annual PAH loading would be extrapolated from the 2.5 month accumulation as ~90 kg year^{-1}. A large part of this loading will fall on pervious areas and may become immobilized.

Evaluation of Observed Data

Although the PAH concentrations in the study area exceed the typical levels reported for other urban areas, the significance of such results needs to be evaluated using the existing water quality criteria. Such an evaluation is hampered by the limited number of PAH substances studied and the limitations of the existing water quality criteria, which are available for a limited number of individual PAHs or their groups, and some of these criteria are common for a number of substances of widely varying properties. Notwithstanding the above limitations, some water quality criteria or standards were found in the literature for seven of the PAH substances studied and these are listed in Table 4.

Toxicity criteria for freshwater aquatic life are listed in Table 4 for two of the substances studied, acenaphthene and fluoranthene. For both substances, the highest levels observed were several orders of magnitude below the chronic toxicity criterion. The criteria for human health imply ingestion of contaminated water and organisms, at certain daily rates, over a lifetime period. Although it would be unrealistic to assume such an intentional use of urban stormwater, there may be a possibility of contamination of drinking water supplies by runoff and, in any case, these criteria offer some guidance in assessing the contamination level. With the above caution in mind, it is noted that the WHO and U.S. EPA drinking water standards, for the Borneff group of PAHs, are exceeded in snowmelt from the study area by more than six times. Similarly, the EPA carcinogenic criteria, at the 10^{-5} risk level, would be exceeded by all four substances listed in Table 4.

Summary of Snowpack Study Findings

Urban snowpack accumulates depositions of PAHs from various sources. Expedient surveys of such accumulations can serve to obtain an approximate evaluation of PAH depositions from diffuse sources and aid in determining areal distribution. Isoloading contours of PAHs stored in the snowpack reflect PAH sources in the area and predominant wind transport. The highest loading in the study area occurred immediately west of the steel plant. The average deposition rates calculated for the study area exceeded the typical data reported for urban areas and, consequently the concentrations of PAHs in the meltwater were also relatively high. Nevertheless, it was observed that the existing water quality criteria for aquatic life have not been exceeded by any of the PAHs studied. The EPA carcinogenic criteria, at the 10^{-5} risk level, have been exceeded by acenaphthene, benzo[a]-pyrene, benzo[k]fluoranthene and fluoranthene. Similarly, the drinking water criterion of 0.2 $\mu g/L^{-1}$ for the sum of the six Borneff PAHs has been exceeded. Realistically, as long as the urban snowmelt and stormwater do not directly contaminate the drinking water supplies, the excesses of the last two compounds are not alarming, because of large dilution in the receiving waters.

STUDIES OF PAHs IN URBAN RUNOFF 1987-88

One of the limitations of the initial PAHs investigations was the limited number of substances studied and the limited number of sampling sites. Consequently, such shortcomings were remedied by further investigations PAHs in surface runoff using the extended list of substances given in Table 1 and additional sampling sites. Data from these investigations are still being analyzed, but the essential findings are presented below.

Procedures

In this phase of the study, additional sampling sites were established and both unfiltered stormwater and sediment samples were collected at a number of sites. These sampling sites are listed below and shown in Figure 1.

Site Number	Location	Medium Sampled
SSMW.1	Metzger St.	Surface runoff
SSMW.2	Connaught Ave.	Surface runoff
SSMW.3	Hill St.	Surface Runoff
SSMW.4	Algoma site	Wet-weather flows in E. Davignon Cr.
SSMW.5	Railway Line	Stormwater in a sewer
SSMS.1	Hill St.	Street sediment
SSMS.2	Wawanosh & Elmw.	Street sediment
SSMS.3	Connaught Ave.	Street sediment
SSMS.4	Metzger St.	Street sediment
SSMS.5	Algoma site	E. Davignon Creek sediment
SSMS.6	Group of sites	Street sediment at a number of sites during a single survey

The collected samples were analyzed for 17 PAHs listed earlier in Table 1. It was noted that several of these substances were never detected above the detection limit and were of secondary importance, because they do not appear on the EPA list of priority pollutants. Consequently, these substances were deleted from further analysis and only 13 substances are reported on. Among these 13, the 6 in the Borneff (WHO) group, including benzo[a]pyrene, are particularly important. A preliminary analysis of data indicated that a probabilistic approach to data interpretation will be most appropriate and further justifications of adopting this approach follow.

PAHs in Urban Runoff - General Findings

PAHs are commonly found in urban runoff and may be transported in any of the following three modes - in the dissolved phase, adsorbed onto the sediment and dissolved in organic matter adhering to the sediment (e.g., crankcase oil). These three modes of transport help to explain the field data collected in this study as well as those reported in other studies (Herrmann, 1981).

PAHs transport by sediment is a particularly important means of transport. It was noted that water samples, which were filtered using a glass-fiber filter with pore size of 0.7 µm, carried just about 10% of the PAHs load observed in unfiltered samples. Similar ratios were reported by Herrmann (1981) and Hoffman et al. (1984). Thus, PAHs found in unfiltered stormwater samples are mostly carried by the sediment. The above water/sediment partitioning may also be affected by the level of PAHs in the sample; this ratio seems to decrease with increasing PAH levels.

Analysis of sediment samples revealed that for street sediment, there is no strong affinity of PAHs to fine fractions. In fact, the total loads were almost equally divided among the fractions $D < 45$ µm, $45 < D$ 250 µm and 250 µm $< D < 1{,}000$ µm, where D is the particle diameter. In the E. Davignon Creek, the smallest particles ($D < 45$ µm) carried about 90% of the total load. It appears from the sediment data that large quantities of PAHs in street sediment are attached to the sediment by other means than sorption.

Assuming that the PAH levels are primarily associated with sediment, correlations between the observed PAH levels and suspended solids levels in these samples and/or organic carbon were tested. The calculated correlations were rather low ($r < 0.5$) and indicate that a more complex relationship between PAHs and sediment, probably affected by particle size distributions and PAH levels in the sediment, exists.

In summary, the levels of PAHs in unfiltered water samples seem to be affected by the presence of sediment, its particle size distribution, and the level of contamination of sediment. Under such circumstances, the PAH levels will not be necessarily correlated with land use, as reported before by Hoffman et al. (1984). One of the reasons for this lack of correlation being that the sources of PAHs are rather numerous and dispersed throughout the urban area. In the case discussed, the primary sources of PAHs include emissions from the steel plant, vehicular traffic, and possibly domestic heating. Among these sources, the plant emissions may show a distinct spatial distribution, but the others are very much dispersed through the urban area. Consequently, it was decided to group all the PAH data together and adopt a statistical approach in their analysis.

Statistical Evaluation of Observed Data

The newly collected data were used to calculate arithmetic means, geometric means, and 10 and 90% exceedance levels. Generally, it is recommended to use the arithmetic mean in loading calculations and the exceedance levels in evaluation of exceedance of water quality criteria. The arithmetic means were calculated for the group of 13 PAHs studied, the six WHO PAHs (the Borneff group) and benzo[a] pyrene. Such data were then used to calculate the annual loadings. The arithmetic means were established as 5,900 ng/L for the 13 PAHs studied, 4,200 ng/L for the six WHO PAHs, and 570 ng/L for benzo[a]-pyrene. A summary of statistical data follows.

Substance	Concentrations in unfiltered stormwater (ng/L)			
	10% N.L.[1]	50% N.L.	90% N.L.	Arithmetic mean
Benzo[a]pyrene	60	330	1,700	570
6 WHO PAHs	480	2,400	11,200	4,200
13 PAHs studied	800	3,800	17,000	5,900

[1] Non-exceedance level (e.g., in 10% of samples, the benzo[a]pyrene concentrations were equal to or less than 60 ng/L)

It should be again emphasized that the reported concentrations correspond to unfiltered stormwater samples and most of the reported loadings were carried by sediment.

The above PAH levels can be used to estimate the annual loadings in urban runoff from the City of Sault Ste. Marie. For this purpose, the earlier estimate of the annual urban runoff volume of 13 x 10^6 m^3/yr is adopted. For this volume and the average concentration of suspended solids in the collected samples of 102 mg/L, the corresponding annual loading of solids is 1,300 t/yr. Estimates of annual PAH loadings computed in various ways are presented below.

Annual Loading Estimates (kg/yr)

	UGLCC Study	From Unfiltered Stormwater Samples	From Sediment Samples	From Snowpack Data
Benzo[a]pyrene	--	7	2	4
6 WHO PAHs	--	55	17	13
13 PAHs studied	122-238[1]	77	31	30

[1] Extrapolated loading for 17 PAHs

The accuracy of the estimates produced in the UGLCC study was evaluated as within an order of magnitude. The two values listed represent low and high estimates produced by high variability of data. Those estimates were produced from limited data for the top 12 PAHs indicated in Table 1 and extrapolated to 17 PAHs using correlations from other areas. Although the UGLCC estimates seem to be high in comparison to other data in the listing of loadings, they are within the specified range of accuracy. Loading bias toward high values seems to follow from a small number of sampling stations and very high readings obtained at one of these stations.

Loading estimates from the unfiltered stormwater samples represent the best estimates. They were derived from a fairly representative data set and further verified against the earlier work. It is recommended to use these loadings in further work.

Loading estimates computed from the annual sediment flux and concentration of PAHs in sediment are probably underestimated. This follows from the fact that these loadings neglect any dissolved phase transport (which may represent 10 - 20% of the total) and they also neglect variations in PAH concentrations in dependence on particle size.

The last estimate in the loading table was produced from snowpack accumulations and basically represents areal deposition loadings. It was produced from the deposition data and an assumption that only the PAH particles reaching impervious surfaces will be transported by urban runoff to the receiving water. The extent of impervious areas was estimated as 33% of the total developed area. Therefore, the annual deposition loading over the whole urban area would be about three times larger, but two thirds of this loading may be retained on pervious surfaces and would not reach the receiving water.

In summary, the annual loadings of benzo[a]pyrene, 6 WHO PAHs and the 13 PAHs studied are estimated as 7, 50 and 80 kg/year, respectively. Most of such loadings are carried attached to the sediment. It is estimated that almost one half of such loadings originates from atmospheric depositions.

Bacteriological Contamination

During the summer of 1986, three sets of stormwater grab samples were collected in the study area and submitted for bacteriological analysis. These samples were collected at Hudson Street, Station Mall, and Georgina Street on July 4, July 28 and August 28, 1986, respectively. The locations of these sites are shown in Figure 1. The results of bacteriological analyses are shown below.

	Bacterial Counts per 100 ml		
Site/Date	Total Coliform	Fecal Coli.	Fecal Streptococci
Hudson St./ 04.7.86	120	<4	758
28.7.86	>320[1]	16	6,200 (est.)
28.8.86	68	20	440
Station M./ 04.7.86	36	4	456
28.7.86	>320[1]	108	410
28.8.86	180	120	96
Georgina St./04.7.86	3,200 (est.)	140	2,500 (est.)
28.7.86	>320[1]	11,000	21,400 (est.)
28.8.86	2,200 (est.)	644	240

[1] Not fully quantified data

The bacteriological data collected in the study area are insufficient to produce good estimates of bacteriological pollution. Recognizing that an important source of bacteria in stormwater are cross-connections with sanitary sewers, or simply illicit connections of sources of sanitary sewage, it would be more appropriate to conduct bacteriological surveys at sewer outfalls. In the absence of such data, any inferences about bacteriological pollution should be based on the literature data (Dutka <u>et</u> <u>al</u>., 1978). Bacteriological counts from several Canadian urban catchments show that total coliform counts in stormwater typically range from 1x10^4 to 1x10^5 and fecal coliforms range from 1x10^3 to 7x10^4, per 100 ml. These ranges were then used to estimate the bacteriological loads in stormwater in Sault Ste. Marie. Depending on concerns about the accuracy of such estimates, further verifications by field sampling would be desirable.

Using the typical bacteriological counts, the annual bacteria loads in stormwater from Sault Ste. Marie were estimated as follows:

Parameter	Total Annual Loading Counts (number of organisms/year) Low Estimate	High Estimate
Total Coliform	1.3×10^{15}	1.3×10^{16}
Fecal Coliform	1.3×10^{14}	9.1×10^{15}

The limited field data seem to indicate lower levels of contamination than the literature data, but this comparison is insignificant because of the limited data scope. Before any field verifications are undertaken, it is recommended to use the literature data for loading estimates.

CONCLUSIONS

Urban runoff from Sault Ste. Marie shows signs of pollution typical for runoff from industrial cities. Using a planning level procedure, the levels of selected pollutants in urban runoff and their annual loadings were estimated. The highest loadings were found for chloride, in the order of 10^6 kg/yr, followed by iron (10^5 kg/yr), oil and grease and ammonia (10^4 kg/yr), phosphorus, zinc and lead (10^3 kg/yr), copper, nickel, phenols, PAHs and cadmium (10^2 kg/yr), cyanides and cobalt (10^1 kg/yr), mercury and PCBs (10^{-1} kg/yr), and HCB (10^{-2} kg/yr). For estimating the bacteriological pollution of stormwater, the available data were clearly insufficient and the literature data had to be used. The low and high estimates of the annual total coliform were computed as 10^{15} and 10^{16} of organisms/

year, respectively. Similar estimates for fecal coliform ranged from 10^{14} to 10^{16} of organisms/year.

Loadings in urban runoff were compared to those from point sources. It was noted that urban runoff loadings exceeded or were comparable to those from point sources for the following parameters: cadmium, cobalt, copper, lead, nickel, HCB, PAHs, and PCBs. In general, however, the loadings of such parameters were not excessive. Specific concerns about PAHs pollution led to further studies of PAHs in urban runoff.

Follow up studies of PAHs in urban runoff were done in two stages. In the first stage, depositions of PAHs from atmospheric sources and their retention by snowpack were investigated. It was noted that the steel plant was the main source of such depositions and their distribution was further affected by prevailing winds. Assuming that only depositions collected on impervious areas end up in runoff, they represent about 40% (30 kg/year) of the total flux of PAHs from the study area.

In the second stage, samples of surface runoff and street sediment were collected and analyzed for the full list of 17 PAHs. Three modes of PAH transport by media were noted - in the dissolved phase, adsorbed to the sediment, and attached to the sediment by other means than sorption. The dissolved loadings were the least significant, representing about 10 to 20% of the total. PAHs found in unfiltered stormwater samples were carried mostly by the sediment. Analyses of sediment samples for various particle sizes indicated that the PAH levels did not decrease significantly with increasing particle size. This suggests that some part of the total loading is carried attached to the sediment by other means than sorption.

The annual loadings of PAHs in stormwater were estimated as 80 kg/yr for the group of 13 PAHs, 60 kg/yr for the six WHO PAHs, and 7 kg/yr for benzo[a] pyrene. When comparing the observed PAH levels to the existing water quality criteria, only the exceedance of the WHO drinking water criteria (200 ng/L for the sum of 6 WHO PAHs) was noted. Realistically, as long as the urban stormwater does not directly contaminate the drinking water supplies, such an exceedance is not significant because of large dilution in the receiving waters and the removal of PAHs with sediment settling.

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TABLES AND FIGURES

Table 1. Urban Runoff Constituents Studied

Parameter	Detection Limit (mg/L)	Parameter	Detection Limit (ng/L)
Ammonia (nitrogen)	0.001	Polynuclear Aromatic Hydrocarbons (PAHs)	
Phosphorus (total)	0.001		
Chloride	0.050		
Cadmium[3]	0.001	Indene[1]	50
Cobalt	0.001	1,2,3,4-Tetrahydronaphthalene[1]	50
Copper[3]	0.001		
Iron	0.020	2-Methylnaphthalene	50
Lead[3]	0.001	Quinoline[1]	50
Mercury[3]	0.00002	1-Methylnapthalene	50
Nickel	0.001	2-Chloronaphthalene[1,3]	50
Zinc[3]	0.001	Acenaphthylene[3]	50
Cyanides (total)	0.010	Acenaphthene[3]	50
Oil & Grease	0.1	Fluorene[3]	50
Phenols (total)	0.001	Phenanthrene[3]	50
		Fluoranthene[2,3]	50
	Detection Limit (ng/L)	Pyrene	50
		Benzo(b)fluoranthene[2,3]	100
Hexachlorobenzene (HCB)[3]	0.4	Benzo(k)fluoranthene[2,3]	100
		Benzo(a)pyrene	100
Polychlorinated Biphenyls (total PCBs)[3]	9	Indeno(1,2,3-cd)pyrene[2,3]	100
		Benzo(ghi)perylene[2,3]	100

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[1] Substance levels below detection levels, omitted in final loading calculations for 13 PAHs

[2] WHO (Borneff) group of PAHs

[3] EPA priority pollutant

Table 2. Constituent Concentrations

	Mean Stormwater Concentrations (mg/L)			Point Source Equivalent Concentrations (mg/L)[1]	Annual Loading in Stormwater (kg/yr)
Constituent	Sault Ste. Marie	NWRI Data Base[2]	NURP Data Base[3]	Sault Ste. Marie	Sault Ste. Marie
Ammonia	0.744	--	--	181.5	10,000
Phosphorus	0.309	--	0.330	3.4	4,000
Chloride	285.000	--	--	623.0	3,700,000
Cadmium	0.0060	0.0015	--	0.002	80
Cobalt	0.00035	0.0040	--	0.0	5
Copper	0.0434	0.0270	0.034	0.0228	560
Iron	6.96	--	--	50.6	90,000
Lead	0.0966	0.146	0.144	0.174	1,300
Nickel	0.0313	0.022	--	0.0512	400
Zinc	0.274	0.490	0.160	1.0	3,600
Cyanides	0.0020	--	--	2.0	26
Oil & Grease	2.52	--	--	282	33,000
Phenols	0.0151	--	--	0.286	200
	Mean Stormwater Concentrations (µg/L)			Point Source Equivalent Concentrations (µg/L)	
Mercury	0.029	--	--	0.16	0.4
Hexachlorobenzene	0.00046	0.0089	--	0.0	0.006
Octachlorostyrene	--	--	--	0.0561	--
PCBs	0.0269	0.131	--	0.0	0.4
PAHs	9.0[4]	--	--	19.4[5]	117

[1] Concentrations calculated from point source loadings (Upper Great Lakes Connecting Channels Workgroup 1988) which were divided by the annual volume of stormwater runoff

[2] Data from Marsalek and Schroeter (1984)

[3] Data from U.S. Environmental Protection Agency (1983)

[4] Only the first 12 PAHs listed in Table 1 were studied, the loading was extrapolated to 17 PAHs

[5] The selection of PAH substances analyzed for point sources somewhat differed from those listed in Table 1

Conversions: 1 mg = 10^3 µg = 10^6 ng

Table 3 PAH Concentrations in Snowpack Samples

Substance	PAH Concentrations (µg/l)									
	Station									
	1	2	3	4	5	6	7	8	9	10
Indene	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050
1,2,3,4-Tetrahydronaphthalene	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050
2-Methylnaphthalene	0.100	0.063	<.050	0.051	0.095	0.210	0.145	0.140	0.212	<.050
Quinoline	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050
1-Methylnaphthalene	0.056	<.050	<.050	<.050	0.051	0.118	0.077	0.090	0.169	<.050
2-Chloronaphthalene	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050
Acenaphthylene	<.050	<.050	<.050	<.050	<.050	0.153	0.063	<.050	<.050	<.050
Acenaphthene	0.052	<.050	<.050	<.050	<.050	0.098	<.050	<.050	<.050	<.050
Fluorene	0.093	<.050	<.050	<.050	<.050	0.237	0.059	0.060	0.135	<.050
Phenanthrene	1.540	0.758	0.164	0.188	0.270	3.560	0.500	0.698	0.733	0.159
Fluoranthene	2.950	1.130	0.186	0.226	0.311	7.020	0.509	0.985	0.630	0.215
Pyrene	1.620	0.501	0.112	0.144	0.199	3.750	0.304	0.624	0.405	0.115
Benzo(b)fluoranthene	0.330	<.100	<.100	<.100	<.100	0.647	<.100	0.392	0.210	<.100
Benzo(k)fluoranthene	0.454	0.150	<.100	<.100	<.100	0.990	<.100	0.518	0.238	<.100
Benzo(a)pyrene	0.296	<.100	<.100	<.100	<.100	0.558	<.100	0.379	0.209	<.100
Indeno(1,2,3-cd)pyrene	0.218	<.100	<.100	<.100	<.100	0.496	<.100	0.410	0.247	<.100
Benzo(ghi)perylene	0.203	<.100	<.100	<.100	<.100	0.450	<.100	0.466	0.299	<.100

Table 3 PAH Concentrations in Snowpack Samples Continued

Substance	PAH Concentrations (µg/l)									
	Station									
	11	12	13	14	15	16	17	18	19	20
Indene	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050
1,2,3,4-Tetrahydronaphthalene	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050
2-Methylnaphthalene	<.050	<.050	<.050	<.050	<.050	<.050	0.101	0.251	0.145	0.101
Quinoline	<.050	<.050	<.050	<.050	<.050	<.050	<.050	0.124	<.050	<.050
1-Methylnaphthalene	<.050	<.050	<.050	<.050	<.050	<.050	0.056	0.177	0.085	0.055
2-Chloronaphthalene	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050
Acenaphthylene	<.050	<.050	<.050	<.050	<.050	<.050	0.058	0.089	0.063	<.050
Acenaphthene	<.050	<.050	<.050	<.050	<.050	<.050	<.050	<.050	0.064	<.050
Fluorene	<.050	<.050	<.050	<.050	<.050	<.050	0.063	0.100	0.117	<.050
Phenanthrene	0.199	0.109	<.050	0.134	<.050	0.194	0.681	0.684	1.402	0.365
Fluoranthene	0.327	0.151	<.050	0.163	<.050	0.191	0.821	0.624	1.770	0.366
Pyrene	0.217	0.088	<.050	0.271	<.050	0.113	0.440	0.345	0.907	0.210
Benzo(b)fluoranthene	0.136	<.100	<.100	<.100	<.100	<.100	<.100	<.100	0.159	<.100
Benzo(k)fluoranthene	0.166	<.100	<.100	<.100	<.100	<.100	<.100	<.100	0.237	<.100
Benzo(a)pyrene	0.145	<.100	<.100	<.100	<.100	<.100	<.100	<.100	0.158	<.100
Indeno(1,2,3-cd)pyrene	0.177	<.100	<.100	<.100	<.100	<.100	<.100	<.100	0.149	<.100
Benzo(ghi)perylene	0.210	<.100	<.100	<.100	<.100	<.100	<.100	0.164	0.163	<.100

Table 4. Water Quality Criteria for the PAHs Studied

	WHO drinking water standard[a] ($\mu g\ L^{-1}$)	U.S. EPA criteria ($\mu g\ L^{-1}$)[b]				
		Freshwater aquatic life toxicity		Human health - Ingestion of contaminated water and organisms cancer risk level[c]		
		Acute	Chronic	10^{-5}	10^{-6}	10^{-7}
Acenaphthene		1,700	520	0.028	0.0028	0.00028
Benzo[a]pyrene				0.028	0.0028	0.00028
Benzo[k]fluoranthene				0.028	0.0028	0.00028
Fluroanthene		3,980	620	0.028	0.0028	0.00028
Sum of six Borneff PAHs	0.200					

[a] The World Health Organization standard for European countries and the U.S. EPA standard. For the same group, the Dutch Basic Water Quality Objective is 0.1 $\mu g\ L^{-1}$ for the median value.

[b] After U.S. EPA (1981)

[c] Cancer risk not determined for individual substances, but the above criteria are common for the whole group. Note also that the main human intake of PAHs is likely to be from the air rather than water.

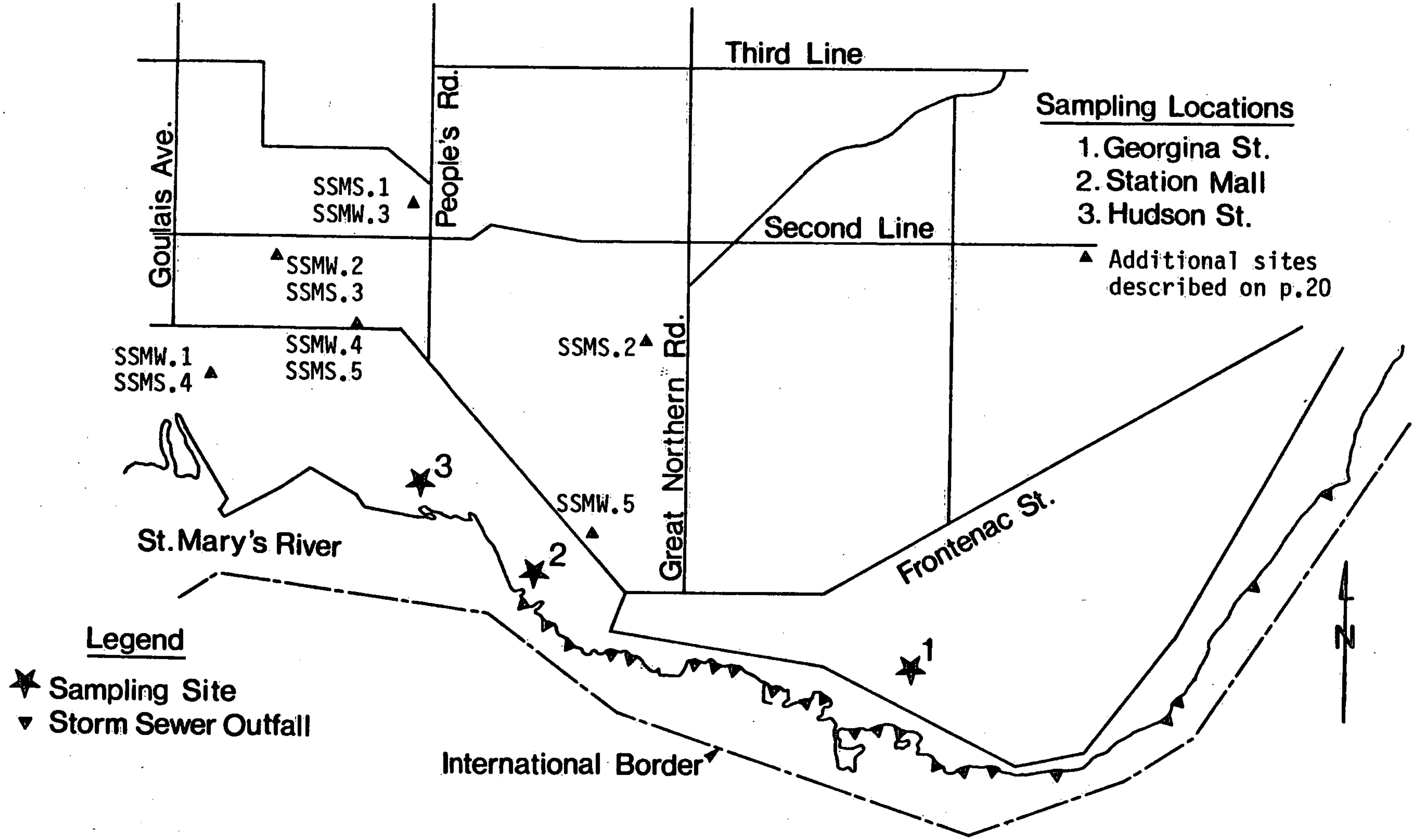

Fig. 1. Storm Sewer Outfalls and Sampling Sites in Sault Ste. Marie.

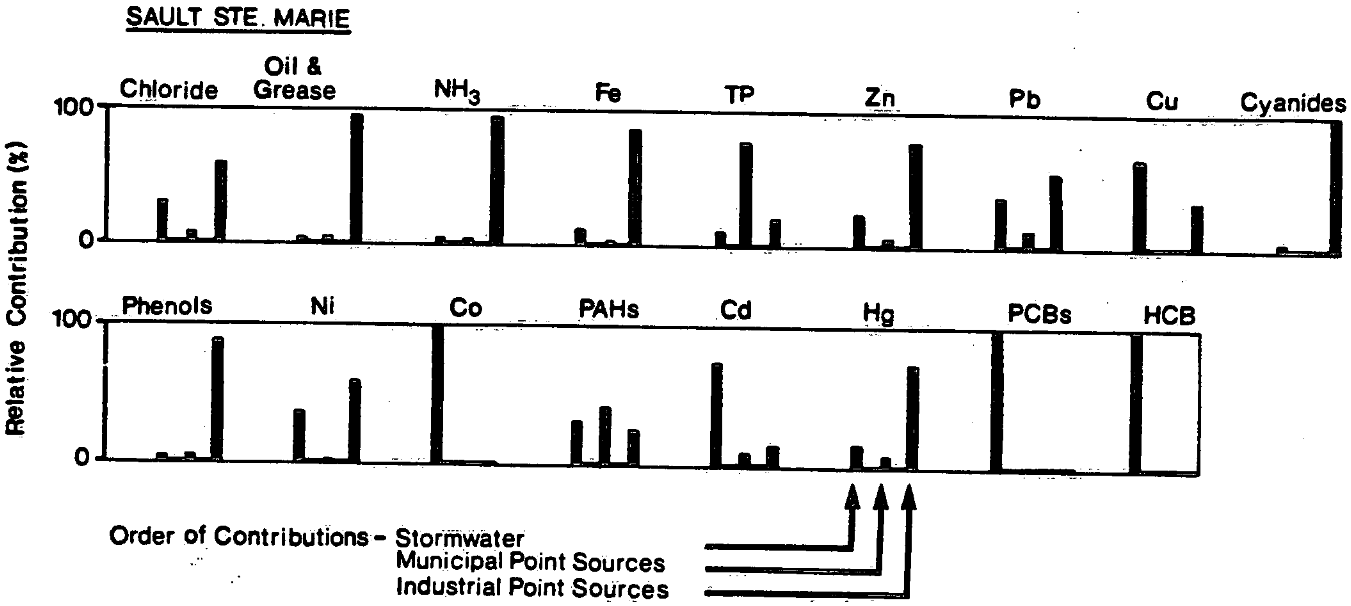

Fig.2. Relative Contributions of Pollution Sources in Sault Ste. Marie

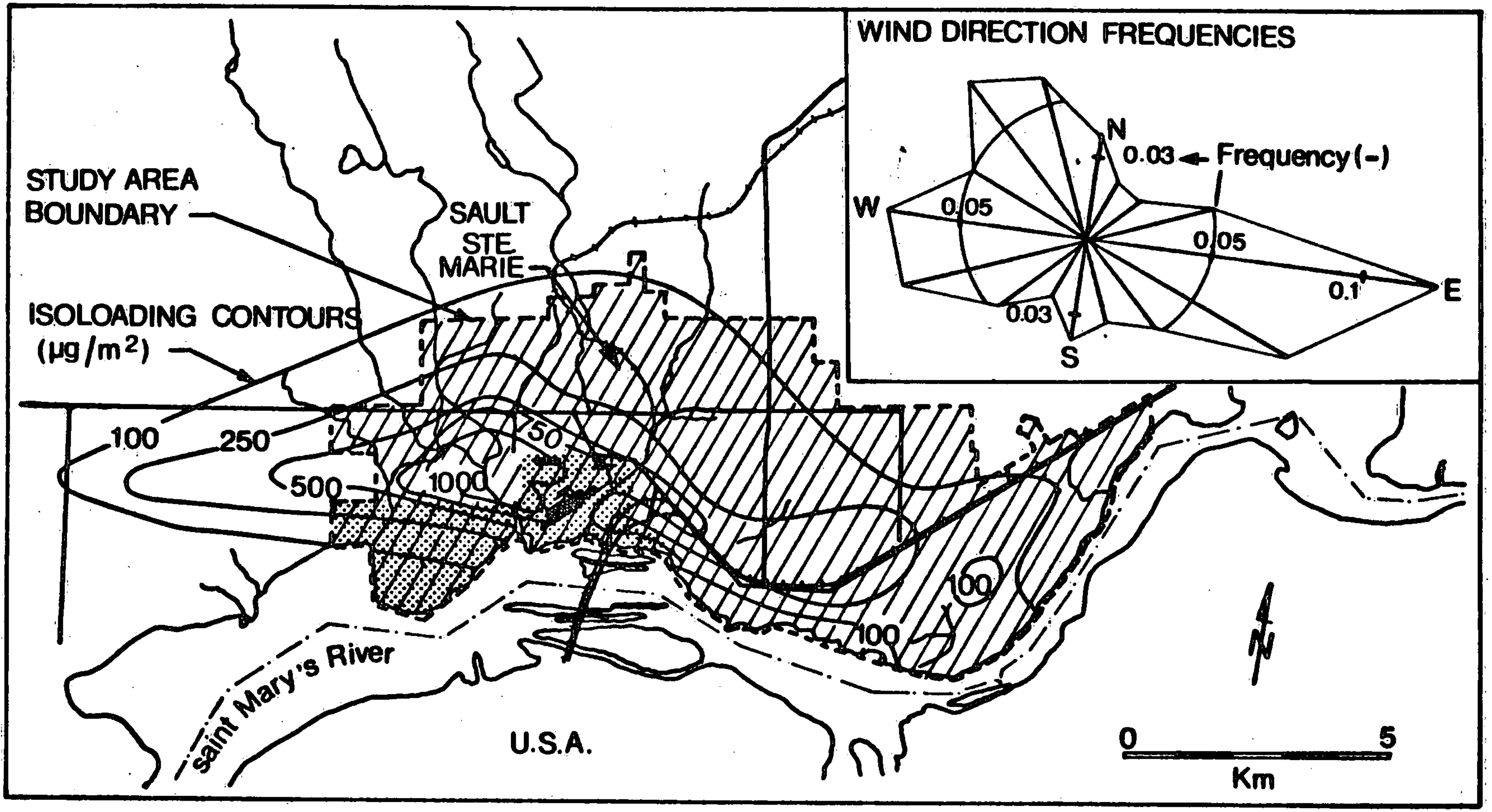

Fig.3. PAH Loading Contours and Wind Direction Frequencies