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ACCUMULATION OF POLYCYCLIC
AROMATIC HYDROCARBONS (PAHs)
IN AN URBAN SNOWPACK

by
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MANAGEMENT PERSPECTIVE

The St. Mary's River has been identified by the Water Quality Board of the International Joint Commission as one of the areas of concern where serious pollutional problems have been repeatedly reported. Some of these problems are caused by elevated levels of polycyclic aromatic hydrocarbons (PAHs) originating from various point and nonpoint sources. Following the earlier evaluation of point sources of PAHs, it was required to evaluate the nonpoint sources as well and, in particular, the PAHs loading in surface runoff from the City of Sault Ste. Marie. Such investigations are currently underway and one of their components, dealing with PAHs accumulation in the snowpack, is described in the report that follows. The general methodology described in the report was found to be relatively inexpensive and highly efficient for determining the nonpoint source and its areal distribution. The same approach could be applied in studies of other persistent substances. The data on PAH accumulation in the snowpack will be used in final evaluations of nonpoint sources of PAHs in the study area. Preliminary analysis indicates that the nonpoint source PAHs loading is comparable to the loading from the point sources and, consequently, should be considered in any remedial action plans.

PERSPECTIVE-GESTION

Le Conseil de la qualité de l'eau de la Commission mixte internationale considère la rivière Sainte-Marie comme un des endroits caractérisés par la récurrence de graves problèmes de pollution. Certains de ces problèmes sont dus aux taux élevés d'hydrocarbures aromatiques polycycliques (HAP) provenant de sources ponctuelles et de sources non ponctuelles. Après l'examen des sources ponctuelles d'HAP, il était nécessaire d'examiner aussi les sources non ponctuelles et, en particulier, la charge en HAP dans les eaux de ruissellement de la ville de Sault-Sainte-Marie. Les travaux sont en cours et ce rapport traite d'une de leurs composantes, à savoir l'étude de l'accumulation d'HAP dans la couverture de neige. La méthodologie générale décrite ici s'est révélée relativement économique et très efficace pour repérer les sources non ponctuelles et leur étendue. Elle pourrait être appliquée à l'étude d'autres substances persistantes. Les données sur l'accumulation d'HAP dans la couverture de neige serviront à l'examen final des sources non ponctuelles de ces substances dans la région étudiée. L'analyse préliminaire indique que la charge d'HAP provenant de sources non ponctuelles est comparable à celle d'HAP provenant de sources ponctuelles; il faudrait donc en tenir compte dans la planification de mesures correctives éventuelles.

RÉSUMÉ

On a étudié l'accumulation d'hydrocarbures aromatiques polycycliques (HAP) provenant de nombreuses sources anthropiques dans une couverture de neige en milieu urbano-industriel. Les valeurs moyennes des charges en HAP dans la couverture de neige ont été déterminées, pointées sur une carte de la zone étudiée et représentées approximativement par des isolignes. Dans la zone urbaine, ces dernières s'étiraient de façon prononcée dans la direction où soufflent les vents dominants. Les taux de dépôt par surface unitaire dans la zone considérée dépassaient les taux habituels mesurés dans d'autres zones urbaines et atteignaient leur valeur maximale immédiatement en aval d'une aciérie. Les niveaux d'accumulation d'HAP en période de fonte de la neige étaient bien inférieurs aux seuils de toxicité pour la vie aquatique en eau douce, mais dépassaient les normes pour l'eau potable de l'OMS et les critères de cancérogénécité de l'EPA (É.-U.) au niveau de risque de 10^{-5}.

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ABSTRACT

Accumulations of polycyclic aromatic hydrocarbons in a snowpack were studied in an industrial urban area with numerous anthropogenic sources of PAHs. Average PAH loadings stored in the snowpack were determined, plotted in a map of the study area, and approximated by isoloading contours. The loading contours were spaced over the urban area with a marked elongation in the direction of prevailing winds. The unit-area deposition rates observed in the study area exceeded the typical rates reported for other urban areas and were the highest immediately downwind of a steel plant. PAH levels in a snowmelt were well below the freshwater aquatic life toxicity criteria, but exceeded both the WHO drinking water standard and the U.S. EPA carcinogenic criteria at the 10^{-6} risk level.

INTRODUCTION

Although the health hazards caused by soot, tar and pitch have been known for more than 200 years, only during the last 50 years have the carcinogenic constituents of those substances been identified as polycyclic aromatic hydrocarbons (PAHs). By 1976, more than 30 PAHs were reported as carcinogens and 17 PAHs were included on the U.S. Environmental Protection Agency (EPA) list of priority pollutants. In the subsequent years, PAHs received much attention regarding their chemical structure, toxicity, reactivity and occurrence in the environment. Although PAHs are commonly reported as a group, the toxicity and relative carcinogenity of individual substances greatly vary (Futoma et al., 1981). Thus, for aggregated PAH data, it is important to specify the substances included in the group.

PAHs are widely distributed in the environment, because of their abundant natural as well as anthropogenic sources. Although no accurate comparisons of loadings from natural and anthropogenic sources were found in the literature, it is generally recognized that the anthropogenic sources prevail (Bjorseth and Ramdahl, 1985) and, worldwide, contribute about 500,000 tonnes of PAHs annually. Typical anthropogenic sources include heating, power generation, industrial processes, incineration and open fire burning, and vehicular transportation (Janssen, 1980).

Many anthropogenic sources of PAHs are concentrated in urban areas where PAH releases are particularly high. Released PAHs are partly deposited within a short distance of the sources and partly

transported by wind to more distant areas depending on the type of release, the location of the release point above the ground, released particle size and wind velocity (Bjorseth and Sortland Olufsen, 1983). Anthropogenic PAHs may reach the surface waters in a number of ways, including wet or dry precipitation, and discharge of urban effluents and surface runoff. Urban effluents conveying PAHs include industrial effluents, particularly process or cooling waters which were exposed to the materials containing PAHs. High levels of PAHs were reported in effluents from such industrial operations as aluminium forming, iron and steel manufacturing, foundries, petroleum refining, and timber products processing (Bjorseth and Ramdahl, 1985; Harrison et al., 1975; U.S. EPA, 1981). PAHs were also found in raw municipal sewage at levels up to 210 µg/l (Borneff and Kunte, 1983). Most of such materials can be removed by proper treatment.

Urban runoff which is conveyed either in the form of stormwater discharges or combined sewer overflows also carries PAHs. The rainwater falling over an urban area may already contain some PAHs, at levels in the order of 1 µg/l (Marsalek and Ng, 1987; Quaghebeur et al., 1983), and such levels are considerably increased when the rainwater contacts urban surfaces with accumulated PAH depositions. Such accumulations are particularly high along roads and highways and may lead to PAH concentrations in highway runoff as high as 15.9 µg/l (Stotz, 1987; van de Ven and Oldenkamp, 1987). Ellis (1986) estimated that 70% of the total PAH loadings reaching streams originate in highway runoff. More general data on PAHs in runoff from about 40 U.S. and Canadian urban areas were reported by Cole et al. (1984) and Marsalek (1986). PAHs were frequently found in runoff at levels up to 12 µg/l. Special conditions occur in the

winter when PAHs accumulate in the urban snowpack and are quickly released in high concentrations during the snowmelt period (Lygren et al., 1984). Concentrations of PAHs in combined sewer overflows may even exceed those in stormwater, because of industrial effluents discharged into combined sewers (Marsalek and Ng, 1987).

PAHs are of special interest in the study area, the City of Sault Ste. Marie, which is characterized by numerous anthropogenic sources of PAHs, particularly those associated with the steel industry, widespread use of wood stoves, and a significant volume of traffic in the City and along the Trans-Canada Highway. Elevated levels of PAHs have been found in the principal water body in the study area, the St. Mary's River. These levels were found in both ambient water and biota, particularly in caged clams. For these reasons and occurrences of other industrial chemicals, the Sault Ste. Marie area has been selected for further investigations under the Municipal-Industrial Strategy for Abatement (MISA) program designed to reduce the input of toxic chemicals into waterways in the Province of Ontario (Ministry of the Environment, 1986).

Investigations of PAHs in urban runoff in the study area started in 1986 and focussed on limited sampling of urban runoff (Marsalek and Ng, 1987). Such investigations excluded the winter period and, to alleviate this limitation, it was decided to undertake a survey of PAHs in the snowpack in the study area. The main objectives of such investigations were to establish areal distributions of PAH depositions in the snowpack and to estimate their contribution to the loadings in surface runoff.

STUDY AREA

The study area represents the land contributing urban runoff within the municipal boundaries of the City of Sault Ste. Marie, which is a city of 83,000 inhabitants located about 500 km northwest of Toronto. The municipal area contributing to urban runoff was estimated as 4,500 ha and, with the exception of rural land along the perimeter, included all the land within the municipal boundaries. The above total area can be subdivided, according to land use, as follows: Residential land - 2,300 ha, institutional land - 300 ha, commercial land 400 ha, industrial land - 600 ha, and open land, 900 ha. The overall area imperviousness was estimated at 26%. The terrain generally slopes toward the St. Mary's River which forms the southern boundary of the city (see Fig. 1).

Urban drainage in Sault Ste. Marie is provided by storm sewers, which discharge either directly into the St. Mary's River, or into several creeks flowing in the north-south direction and discharging into the same river.

The principal water body in the study area is the St. Mary's River which is used for navigation, power generation, water supply, wild life habitat, and transport of stormwater and wastewater effluents. Water quality in the river has been of some concern, particularly the levels of PAHs and some industrial chemicals.

The main industrial operation in the study area is the primary manufacturing of iron and steel by the Algoma Steel Corporation Limited which produces about 2.5 million tonnes of steel annually and employs about 7,000 people. The second largest employer is St. Mary's Paper with about 500 employees.

METHODS

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. It should be noted that this list includes perhaps the most extensively studied and higly carcinogenic PAH substance, benzo(a)pyrene; the six PAHs in the Borneff group, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, 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 which are described later. All the analytical data reported are extractable data for the water-sediment mixtures sampled.

Sampling Sites and Procedures

In the study area, 20 sampling stations have been selected in a grid centred around the steel plant property as shown in Fig. 1. The sampling grid points, which are listed in Table 2, were spaced from 1.2 km to 16 km from the centre. The greatest density of sites followed the east-west direction which is the direction of predominant winds during the sampling period. The sampling stations had to be accessible, somewhat remote from the major traffic routes, and 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. Special care was taken to push the sampler as close to the ground surface as practical. In locations with small snow depths, the whole procedure was repeated until enough snow volume was collected. At each location, the in-situ depth of snow was measured and, in conjunction with the surface area sampled, used to estimate the undisturbed sample volume. Snow samples were then slowly melted and the volume of melt-water was measured. From the above data, it was possible to determine the water equivalent of the snowpack and the depth of water stored. Such information was used in calculations of PAH loadings stored in the snowpack. The melt-water was transferred into laboratory bottles and submitted for analysis.

Basic snowpack data are also listed in Table 2. The depth of snow varied from 0.09 to 0.51 m and such values reflect the below-average snowfall experienced during the 1986/87 winter. The water equivalent data in Table 2 are well above the value of 0.1 corresponding to fresh snow and somewhat below the maximum value of 0.6 observed in ripe snowpacks just before the snowmelt season begins (Chow, 1964). The observed water equivalent values indicate high runoff potential.

Analytical Procedures

All snowmelt samples were extracted by the methylene chloride water extraction procedure. The dehydrated extract was concentrated and further cleaned up using gel permeation chromatography to remove

coextracted interfering compounds. The final extract was analyzed for PAHs using one-column gas chromatography and a flame ionization detector.

RESULTS AND DISCUSSION

PAH Concentrations and Frequencies of Detection

Analysis of the 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 about 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(a)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. Very carcinogenic benzo(a)pyrene was detected at levels of one order of magnitude lower.

It was of interest to compare PAH concentrations in the snowpack against those observed in urban runoff from the same general area. Such concentrations were reported for the sum of 14 PAHs detected in the range from 3 to 12 µg/l (Marsalek and Ng, 1987). The corresponding range of values detected in the snowpack ranged from 1 to 18 µg/l. Thus it appears that there is no significant difference between PAH concentrations in urban runoff and snowmelt water. Relatively high readings of fluoranthene and several other substances were detected in the vicinity of the steel plant and the same substances were found in high concentrations in the plant effluent (Environmental Protection Service, 1986). Air quality data are not available for the study area at this time.

The snowpack PAH data were also compared to the extensive U.S. data collected by Cole et al. (1984) under the National Urban Runoff Program (NURP). In that program, seven of the PAHs listed in Table 3 (fluorene, phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene) were detected in seven of the 15 large cities studied. The detections of individual substances, at levels from 0.3 to 12 µg/l, were relatively infrequent and ranged from 1 to 12%. In that sense, the data in Table 3 represent higher values in terms of both frequencies and levels.

The data from Table 3 were further compared to some limited snowmelt data as shown in Table 4. Such data refer to snow samples collected along the streets and roads in residential, commercial and industrial areas in Windsor, Ontario (Marsalek and Ng, 1987) and from snow banks along a highway in southern Norway (Lygren et al., 1984). For the three PAHs listed in Table 4, the highest concentrations were found in the study area, just west of the steel plant, followed by snow banks along a highway and a commercial area in Windsor with high traffic density. The PAH concentrations in the study area are comparable to those found in locations along a highway, with high PAH deposition rates, and are significantly greater than those reported for Windsor.

The above discussion indicates that the PAH concentrations in the undisturbed snowpack in the study area are comparable to the levels reported for relatively contaminated parts of urban areas. The release of accumulated PAHs during the snowmelt period and its impact on the receiving waters are discussed later.

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 ($\mu g/m^2$), C is the concentration ($\mu g/l$), V is the volume of melt-water (1), and A is the snowpack area sampled (m^2). The calculated loading rates are listed in Table 5.

The loading rates in Table 5 correspond to an accumulation period of 11 weeks and range from 90 to 1,600 $\mu g/m^2$. 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 are shown in Table 5 and their weighted average was only 11% when using the loading rate as a weighting factor.

To evaluate the significance of the loading rates in Table 5, it was of interest to compare them to the data from other urban areas. Such a comparison is presented in Table 6 for weekly deposition rates. For the study area, the weekly deposition rates were calculated by dividing the total loading rates by the accumulation period in weeks, thus neglecting possible losses. It should be also recognized that the accumulation of PAHs in the snowpack and their release vary in time.

The data in Table 6 indicate that the weekly deposition rates determined for the snowpack in the study area, assuming negligible losses, are fairly high and in some parts of the study exceed the typical rates reported for fairly contaminated locations in industrial cities and along a major highway. Furthermore, these high rates do not reflect high PAH depositions in narrow bands along roads (Harrison and Johnston, 1985) which were not sampled in the study area.

The loading rates at sampling points were plotted in Fig. 2 and, using the point data, approximate isoloading contours were derived by linear interpolations among the point data. It was felt that more sophisticated interpolation methods were not justified because of the uncertainties in loading rates and the fact that the loading rates

may depend not only on the location, but also on wind data which could not be readily considered in the interpolations.

The isoloading contours in Fig. 2 generally follow the outline of the urban area studied, except for an 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 reach 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 direction 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 Fig. 2 and clearly shows the predominance of easterly winds which then displace the loading contours in the westerly direction.

The relationship between the loading rates and the prevailing winds was also statistically evaluated. For this purpose, average loadings over a distance of 4 km from the grid centre were determined for all those directions which fell within the study area. These loadings are listed in Table 7.

The highest loadings in Table 7 correspond to the WNW, NW and W directions. A rank correlation coefficient between the mean directional loadings and the wind direction frequency was determined as 0.8 and supports the explanation that the elongation of the loading contours is caused by wind transport.

Fairly fast drop in loading rates with the distance from the steel plant agrees well with the observations of Grimmer (1983a) who reported that at a coke plant in Essen, FRG, the highest PAH depositions were limited to a radius of about 3 km around the plant and, outside of this circle, the depositions dropped to about one third.

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 about 18 kg. The uncertainty in this estimate caused by the data below the detection limit was relatively low, about 10%. A similar calculation for the Borneff group of six PAHs produced their loading in the snowpack as 8 kg.

Accumulations of PAHs in urban snowpacks provide a good preliminary indication of deposition of PAHs from diffuse urban sources. Such accumulations can be investigated fairly expediently and inexpensively. In the case under discussion, this approach clearly indicated the impact of steel plant emissions and air transport on PAH depositions. Calculations of mean deposition rates from the accumulated loadings involve a number of uncertainties, including those caused by errors in the estimation of the accumulation period, sampling errors, and possible PAH losses in the snowpack. Sampling errors caused by spatial variations in data could be reduced by sampling in two stages. The results of the first stage could be used to design a more efficient network of sampling sites for the second stage. No information on PAH losses in the snowpack

was found in the literature. It was noted, however, that fate processes important for PAHs in aquatic systems, such as photolysis of dissolved PAHs and bioaccumulation and biodegradation (Versar, 1979), either do not occur at all or are severely impeded in the snowpack. Therefore, PAH losses in the snowpack should be minimal. It was reported by Lygren et al. (1984) that PAHs stored in the snowpack are quickly released during the snowmelt period and thereby create a shock loading on the receiving waters. In fact, the bulk of the snowpack could melt in one week. The average concentration of PAHs in fully mixed melt-water from the study area was estimated as 3 µg/1.

The PAH accumulations in snowpack could be also used to estimate annual depositions. Although the data on hand refer to the winter conditions, Seifert and Lahmann (1980) showed that in industrial urban areas there are no seasonal variations in PAH depositions. Using this assumption, the PAH loading corresponding to a 2.5 month accumulation would be extrapolated as about 90 kg/year. 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 listed in Table 8.

Toxicity criteria for freshwater aquatic life are listed in Table 8 for two of the substances studied, acenaphthene and fluoranthene. For both substances, the highest observed levels 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^{-6} risk level, would be exceeded by all four substances listed in Table 8.

Sources

The study area is characterized by numerous sources of PAHs including industrial emissions, domestic heating and automobile exhausts. The areal distribution of PAH loadings in the snowpack

tends to indicate that industrial emissions are the main source of PAHs, with the highest loadings observed immediately downwind from the steel plant. This tendency was further investigated by the fingerprinting technique. In this technique, the levels of individual substances are related to the level of a reference substance from the same group, and the resulting sets of relative concentrations, fingerprints, are compared (Grimmer, 1983b). Using pyrene as the reference substance, the fingerprinting technique was applied to the snowmelt data collected in the study area. The resulting fingerprint graphs, with 95% confidence intervals, are shown in Fig. 3 for six stations with practically all the data above the detection level. The PAH abbreviations used in Fig. 3 were defined earlier in Table 1.

For the first seven PAHs on the left-hand side, all the stations yielded similar fingerprints. For the six PAHs of Borneff, there are statistically significant differences between two groups of stations. The first group, which includes stations 1, 6 and 19, represents the area immediately west of the steel plant with some of the highest depositions. The second group, which includes stations 8, 9 and 11, represents the area located east of the steel plant. The comparison of fingerprints for these two areas indicates some differences in sources, with the westerly stations dominated by steel plant emissions and the easterly stations being influenced by other urban sources. The available data did not allow further differentiation among the sources. An average fingerprint of the stormwater data collected in the eastern part of the study area earlier, with its 95% confidence intervals, is also shown in Fig. 3.

Similarities between the fingerprints for snowmelt and stormwater in the area east of the steel plant indicate the same origin of contamination. The PAH fingerprints in Fig. 3 show that the identification of sources by fingerprinting is not very effective if the statistical distributions of data with appreciable scatter are considered.

CONCLUSIONS

Urban snowpack accumulates depositions of PAHs from various sources. Expedient surveys of such accumulations can serve for approximate evaluation of PAH depositions from diffuse sources and their areal distribution. Isoloading contours of PAHs stored in the snowpack reflect PAH sources in the area and predominant wind transport. The highest loadings 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 melt-water were also relatively high. Nevertheless, it was observed that the existing water quality criteria for aquatic life have not been exceeded by any PAHs studied. The EPA carcinogenic criteria, at the 10^{-6} risk level, have been exceeded by acenaphthene, benzo(a)pyrene, benzo(k)fluoranthene and fluoranthene. Similarly, the drinking water criterion of 0.2 µg/l 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 last two exceedances are not alarming, because of large dilution in the receiving waters.

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REFERENCES

Bjorseth, A. and T. Ramdahl. 1985. Sources and emissions of polycyclic aromatic hydrocarbons. In: Bjorseth, A. and T. Ramdahl, eds., Handbook of polycyclic aromatic hydrocarbons, Vol. 2. Marcel Dekker Inc., New York, N.Y., pp. 1-20.

Bjorseth, A. and B. Sortland Olufsen. 1983. Long range transport of polycyclic aromatic hydrocarbons. In: Bjorseth, A. ed., Handbook of polycyclic aromatic hydrocarbons. Marcel Dekker Inc., New York, N.Y., pp. 507-523.

Borneff, J. and H. Kunte. 1983. Polycyclic aromatic hydrocarbons in river and lake water, biota and sediments. In: Bjorseth, A. ed., Handbook of polycyclic aromatic hydrocarbons. Marcel Dekker Inc., New York, N.Y., pp. 629-652.

Chow, V.T. 1964. Handbook of applied hydrology. McGraw-Hill Book Company, New York, N.Y.

Cole, R.H., Frederick, R.E., Healy, R.F. and R.G. Rolan. 1984. Preliminary findings of the priority pollutant monitoring project of the Nationwide Urban Runoff Program. J. PWCF, 56: 898-908.

Ellis, J.B. 1986. Pollutional aspects of urban runoff. In: Torno, H.C., Marsalek, J. and M. Desbordes, Eds., Urban runoff pollution. Springer-Verlag, Heidelberg, FRG, pp. 1-38.

Environmental Protection Service. 1986. Industrial effluent screening survey. The Algoma Steel Corporation Limited, Sault Ste. Marie, Ontario (Data Summary Report). Environmental Protection Service, Toronto, Ontario.

Futoma, D.J., Smith, S.R., Smith, T.E. and J. Tanaka. 1981. Polycyclic aromatic hydrocarbons in watersystems. CRC Press, Boca Raton, Florida.

Grimmer, G. 1983a. Environmental carcinogens: polycyclic aromatic hydrocarbons. CRC Press, Boca Raton, Florida.

Grimmer, G. 1983b. Profile analysis of polycyclic aromatic hydrocarbons. In: Bjorseth, A., Ed., Handbook of polycyclic aromatic hydrocarbons. Marcel Dekker Inc., New York, N.Y., pp. 149-181.

Harrison, R.M., Perry, R. and R.A. Wellings. 1975. Polynuclear aromatic hydrocarbons in raw, potable and waste water. Water Res., 9: 331-346.

Harrison, R.M. and W.R. Johnston. 1985. Deposition fluxes of lead, cadmium, copper and polycyclic aromatic hydrocarbons on the verges of a major highway. Sci. Total Environ., 46: 121-135.

Janssen, O. 1980. Brief review on polycyclic aromatic hydrocarbons in vehicle exhaust. In: Luftverunreinigung durch polycyclische aromatische Kohlenwasserstoffe. V.D.I. Berichte Nr. 358, Duesseldorf, pp. 69-79.

Johnston, W.R. and R.M. Harrison. 1984. Deposition of metallic and organic pollutants alongside M6 motorway. Sci. Total Environ., 33: 119-127.

Lygren, E., Gjessig, E. and L. Berglind. 1984. Pollution transport from a highway. Sci. Total Environ., 33: 147-159.

Marsalek, J. 1986. Toxic contaminants in urban runoff: a case study. In: Torno, H.C., Marsalek, J. and M. Desbordes, Eds., Urban runoff pollution. Springer-Verlag, Heidelberg, FRG, pp. 39-58.

Marsalek, J. and H.Y.F. Ng. 1987. Contaminants in urban runoff in the Upper Great Lakes Connecting Channels area. National Water Research Institute, Burlington, Ont., Unpublished Report No. RRB-87-27.

Ministry of the Environment. 1986. Municipal-Industrial Strategy for Abatement. Ministry of the Environment, Toronto, Ontario.

Quaghebeur, D., de Wulf, E., Ravelingen, M.C. and G. Janssens. 1983. Polycyclic aromatic hydrocarbons in rainwater. Sci. Total Environ., 32: 35-54.

Seifert, B. and E. Lahmann. 1980. Luftstaub-Untersuchungen mit der Hochleistungs-Fluessigkeits-Chromatographie. In: Luftverun-reinigung durch polycyclische aromatische Kohlenwasserstoffe, V.D.I. Berichte Nr. 358, Duesseldorf, pp. 127-131.

Stotz, G. 1987. Investigations of the properties of the surface water runoff from federal highways in the FRG. Sci. Total Environ., 59: 329-337.

U.S. Environmental Protection Agency. 1981. Treatability manual. Vol. I - Treatability data. U.S. EPA, Washington, D.C., EPA-600/2-82-001a.

van de Ven, F.H.M. and A. Oldenkamp. 1987. Kwaliteit van de afgevoerde neerslag van een hoofdweg in Lelystad. H_2O, 20: 148-151.

Versar, Inc. 1979. Water-related environmental fate of 129 priority pollutants. U.S. Environmental Protection Agency, Washington, D.C., EPA-440/4-79-029b.

Table 1   PAH Substances Studied

Substance	Adopted Abbreviation	Detection Limit (µg/l)	Borneff Group	EPA Priority Pollutant
Indene	---	.050		
1,2,3,4-Tetrahydro- naphthalene	---	.050		
2-Methylnaphthalene	2-MNA	.050		
Quinoline	QUI	.050		
1-Methylnaphthalene	1-MNA	.050		
2-Chloronaphthalene	---	.050		x
Acenaphthylene	ANY	.050		x
Acenaphthene	ANE	.050		x
Fluorene	F	.050		x
Phenanthrene	PA	.050		x
Fluoranthene	FL	.050	x	x
Pyrene	P	.050		x
Benzo(b)fluoranthene	BbF	.100	x	x
Benzo(k)fluoranthene	BkF	.100	x	x
Benzo(a)pyrene	BaP	.100	x	x
Indeno(1,2,3-cd)pyrene	IP	.100	x	x
Benzo(ghi)perylene	BghiP	.100	x	x

Table 2   **Sampling Station Locations and Snowpack Data**

Station Number	Grid Location		Land Use Zoning	Snow Depth (m)	Water Equivalent (-)
1	3	km W	Industrial	0.27	0.35
2	3	km WNW	Vacant	0.38	0.29
3	3	km N	Vacant	0.42	0.29
4	3	km NE	Park Land	0.47	0.27
5	3	km E	Residential	0.35	0.30
6	1.5	km W & WNW	Residential	0.21	0.41
7	1.5	km SE & ESE	Industrial	0.17	0.32
8	3	km ESE	Industrial	0.27	0.32
9	3	km SE	Park Land	0.09	0.25
10	6	km E	Vacant	0.32	0.30
11	8.4	km ESE	Residential	0.21	0.30
12	9	km E	Rural Area	0.44	0.25
13	9	km N	Rural Area	0.51	--
14	9	km W	Rural Area	0.33	0.28
15	16	km E	Rural Area	0.46	--
16	7.5	km ESE	Residential	0.35	0.27
17	1.2	km NE	Residential	0.32	0.38
18	1.4	km NNW	Residential	0.27	0.35
19	3	km W	Industrial	0.25	0.39
20	1.8	km SE	Institutional	0.39	0.31

Table 3   PAH Concentrations in Snowpack Samples

PAH Concentrations (μg/l)

Substance	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

PAH Concentrations (μg/l)

Substance	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 6   Comparison of Deposition Rates

Substance	Weekly Deposition Rates (µg/m²/week)			
	Study Area[1]	Three German Cities[2]	England, Motorway M6[3] Within 4 m	Background
Fluoranthene	1.5 – 68	4.5 – 15.4	15.2	0.14 – 0.33
Phenanthrene	2.2 – 34	–	–	–
Pyrene	0.9 – 37	2.7 – 9.8	–	–
Benzo(a)pyrene	0.5 – 5.5	0.5 – 2.0	4.9	<.001 – 0.022

[1]Background stations with all data below the detection level excluded

[2]After Seifert and Lahmann (1980); mean values for Berlin, Frankfurt and Duesseldorf

[3]After Johnston and Harrison (1984)

Table 4   Comparison of PAH Concentrations in Snow from Various Areas

PAH Substance	PAH Concentrations (µg/l)		
	Study Area	Highway Snow Banks[1]	Street Snow Banks[2]
Phenanthrene	0.1 - 3.6	4.1 - 6.8	0.4 - 2.7
Fluoranthene	0.2 - 7.0	1.8 - 3.1	0.7 - 3.4
Pyrene	0.1 - 3.8	1.9 - 3.1	0.5 - 2.8

[1]After Lygren et al. (1984)

[2]After Marsalek and Ng (1987)

Table 5   PAH Loading Rates at Sampling Points

Station	Loading Rates of PAHs Studied ($\mu g/m^2$)	Uncertainty Due to Data Below Detection Limit (%)
1	784	2
2	328	13
3	116	51
4	134	43
5	143	31
6	1598	1
7	110	19
8	430	3
9	79	4
10	92	49
11	114	12
12	90	58
13	---	--
14	97	46
15	---	--
16	93	49
17	315	15
18	274	11
19	366	2
20	123	28

Table 7   PAH Deposition and Wind Frequency Rankings

Areal Deposition Ranking	Direction	Mean Unit Deposition ($\mu g/m^2$)	Wind Frequency Ranking
1	WNW	820	2
2	NW	760	7
3	W	720	1
4	NNW	490	10
5	E	410	3
6	N	390	9
7	ENE	380	4
8	NNE	370	11
9	NE	360	8
10	WSW	340	6
11	ESE	300	5

Table 8   Water Quality Criteria for the PAHs Studied

| | WHO Drinking Water Standard[1] (µg/l) | U.S. EPA Criteria (µg/l)[2] | | | | |
| | | Freshwater Aquatic Life Toxicity | | Human Health – Ingestion of Contaminated Water and Organisms Cancer Risk Level[3] | | |
		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
Fluoranthene		3,980	620	0.028	0.0028	0.00028
Sum of 6 Borneff PAHs	0.200					

[1]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 µg/l for the median value.

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

[3]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.
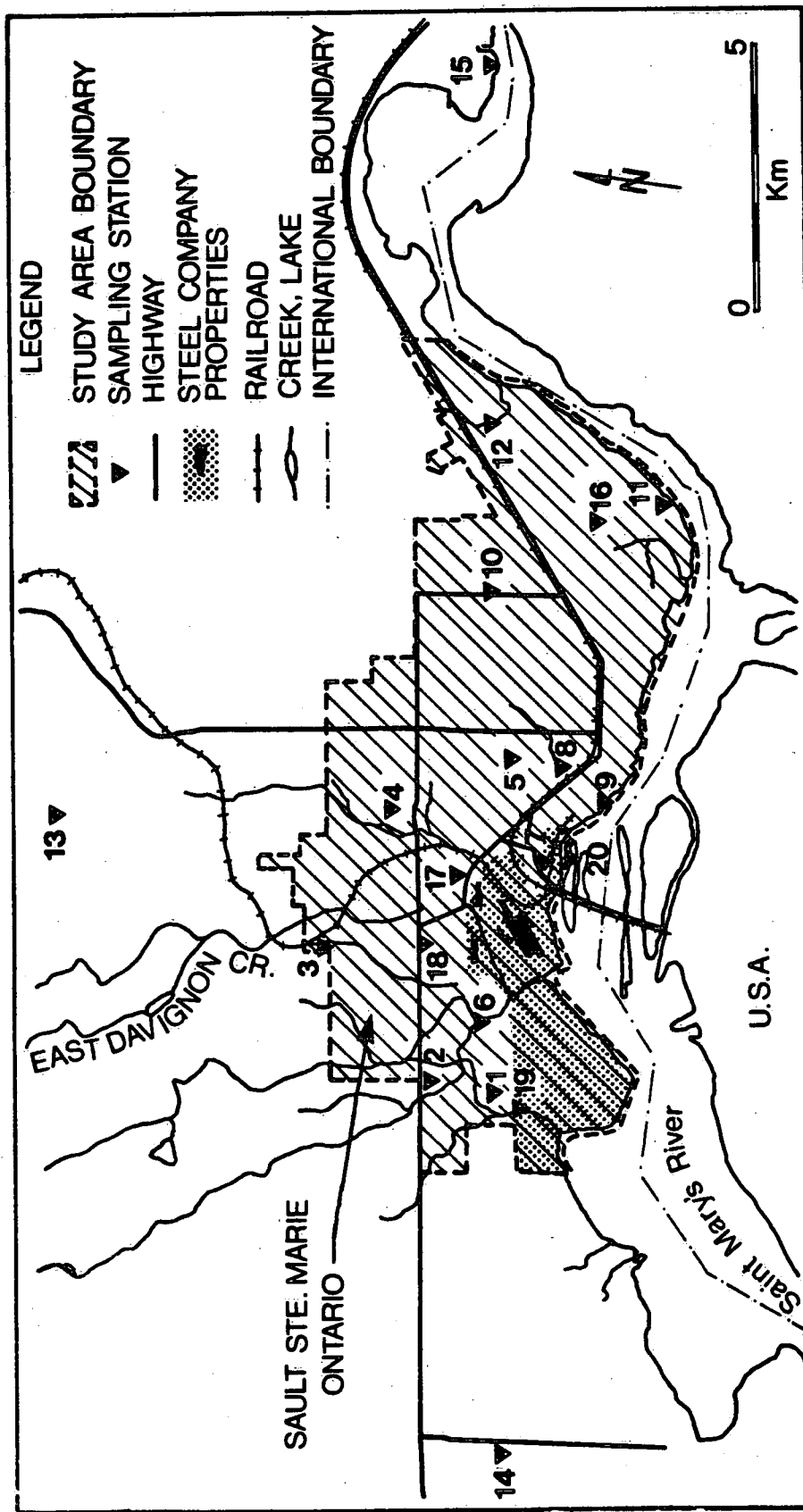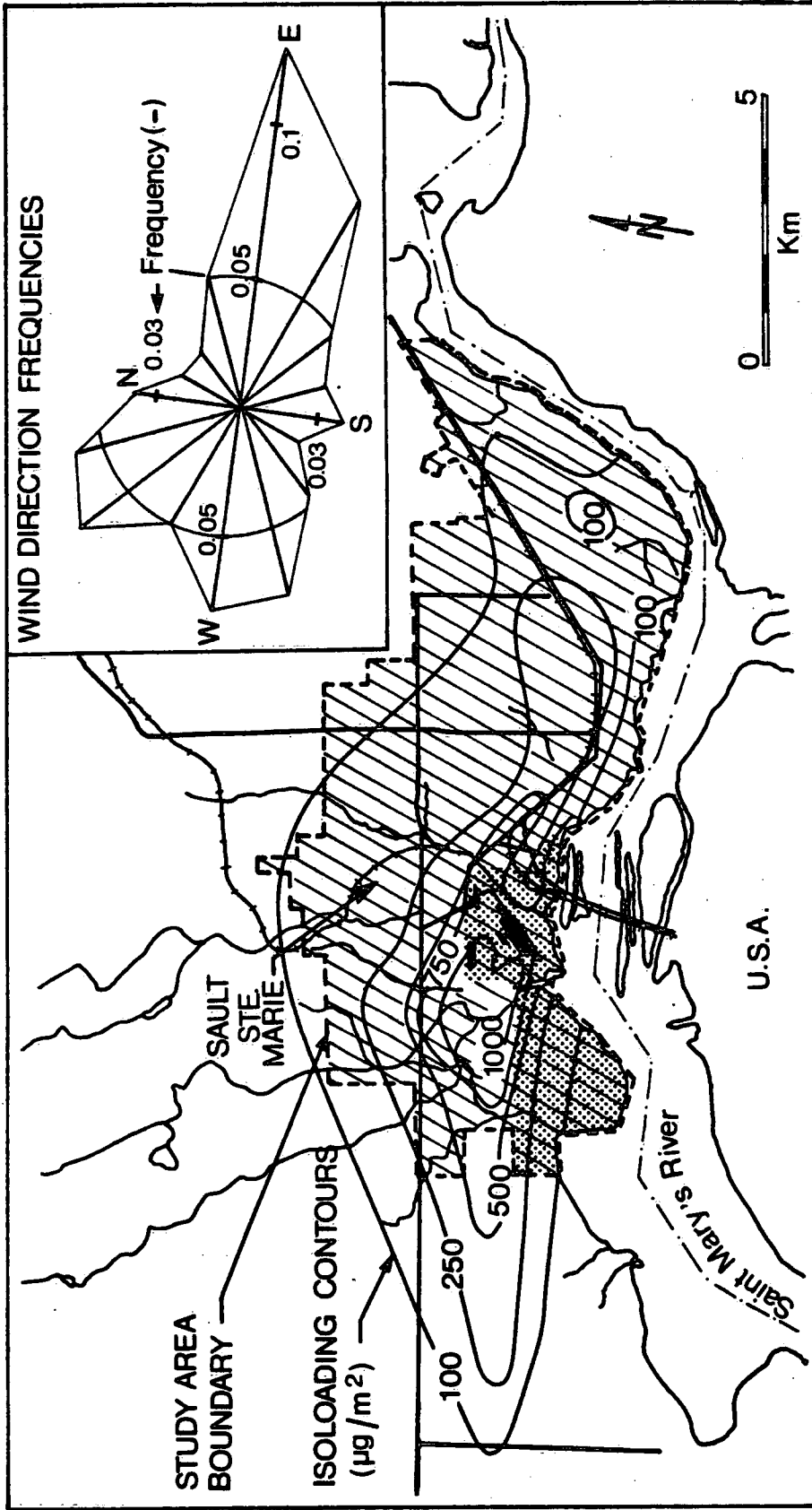
Fig.1. Map of the Study Area

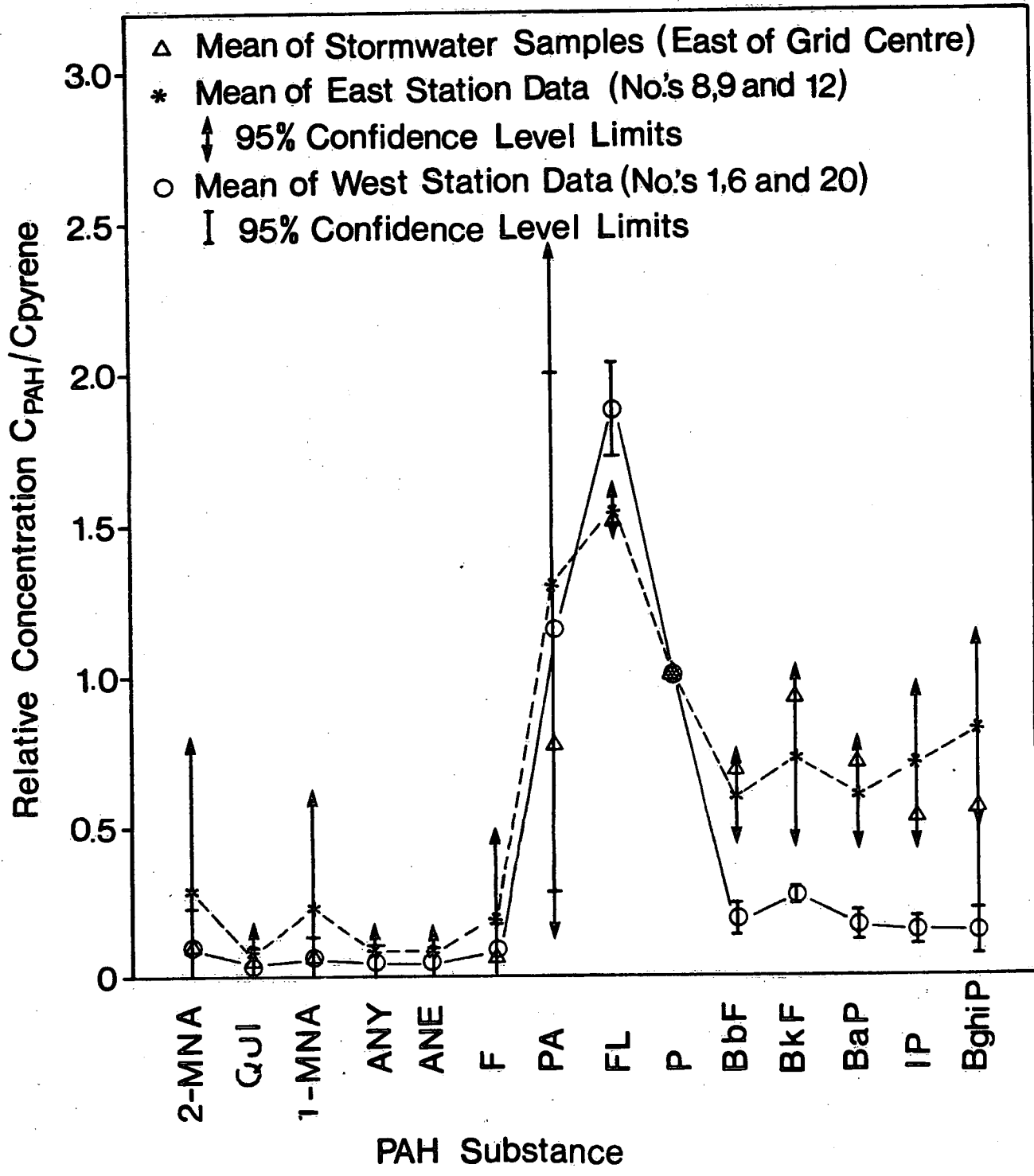Fig.2. PAH Loading Contours and Wind Direction Frequencies

Fig.3. PAH Fingerprints