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in Contaminated Sediments

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POTENTIALLY SIGNIFICANT UNDERESTIMATION OF PAHs
IN CONTAMINATED SEDIMENTS

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ABSTRACT

Freshwater and marine sediment samples collected for analysis of trace organic contaminants are frequently freeze dried and then stored, either cold or at ambient temperatures, sometimes for years, before extraction and analysis. The potential for loss of up to 99% of naphthalene was observed during the analysis of coal tar contaminated sediments from Hamilton Harbour, Lake Ontario. Investigations revealed that inadequate temperature control and excessive total exposure time during freeze drying produced large and highly variable losses of naphthalene and much smaller losses of higher molecular weight PAHs. Such under reporting of naphthalene may lead to serious underestimation of the acute toxicity of sediments to benthic fauna.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in all compartments of the environment, reflecting their biogenic and natural combustion origins (Blumer, 1976). Human industrial activities in this century have resulted in localized high discharges which tends to accumulate in the sediments of lakes and streams (Laflamme and Hites, 1978). The combustion of fuels in power production, space heating and in internal combustion engines produces PAHs that are widely dispersed on airborne particles, much of which also ends up in sediments.

The carcinogenic potential of PAHs is well established and is highest for specific compounds with four or more aromatic rings; no effects are observed with diaromatic PAHs

(Brown and Weiss, 1978). Acute toxicity manifestations tend to follow the the opposite trend with the highest toxicity observed naphthalene and its methylated derivatives (Heitkamp et al., 1987).

As a laboratory providing specialty trace organic analyses on environmental samples to several research groups studying the effects of organic contaminants on aquatic ecosystems, the authors frequently receive sediment samples processed in a variety of ways without prior consultation. The most common treatment is freeze drying followed by storage in sealed opaque glass or plastic containers at room temperature. While conducting a study on the toxicity of a coal tar spill in Hamilton Harbour to benthic organisms, low and highly variable naphthalene recoveries from freeze dried sediment samples were observed. Further investigation showed much higher recoveries of naphthalene using more appropriate sediment treatment. Higher molecular weight PAH compounds were much less severely affected. Thus, the goal of this study was to inspire sample treatment appropriate to the analytical objectives.

Hamilton Harbour, situated at the western end of Lake Ontario, is one of 42 Great Lakes Areas of Concern (International Joint Commission, 1987). A major factor in this designation, is the presence of sediments which are highly contaminated with PAHs as a result of historical spills of coal tar from coking operations at two large steel mills (Rodgers et al, 1988).

EXPERIMENTAL

Sediment core samples for this study were collected from the coal tar 'hot spot' in Hamilton Harbour (Figure 1) during the summer of 1990 using a Benthos corer. The cores were sectioned at 2 cm intervals immediately after collection. All samples and subsamples were frozen intact within 4 hours of collection. Samples to be freeze dried were thawed, blended, subsampled and refrozen immediately prior to freeze drying. The samples were freeze dried in a large common user facility along with unrelated samples for approximately one week. Similarly, samples to be 'wet' extracted, were thawed, blended, and subsampled. Excess water was removed from the wet extraction subsamples by decanting and absorption on a pad of glass fibre filters. The partially dried subsample was then blended with anhydrous sodium sulphate. Both sample treatments were then Soxhlet extracted with dichloromethane for 12 hours. All extracts were concentrated by rotary evaporation at 20°C with solvent exchange to 1 mL isoctane, cleaned up on Florisil minicolumns and analysed in toluene solution by selected ion GCMS for 18 selected PAHs on a 30 m x 0.255 mm Durabond DB5 fused silica column.

RESULTS AND DISCUSSION

Numerous surficial sediments and sectioned cores were collected in 1989 and 1990 from a nearshore area in Hamilton Harbour where extensive coal tar spills and discharges from coking operations had accumulated over a number of years. At many of the less contaminated sites, the naphthalene concentrations were in the same range as other individual PAHs but at the most contaminated sites, especially deeper in the core samples, naphthalene concentrations were an order of magnitude higher. Core sections at 10-12 cm

from three of these sites (Fig. 1) were chosen to examine naphthalene losses due to freeze drying and are illustrated graphically in Fig. 2. The concentrations of 18 selected PAHs from one of these sites are shown in Table 1.

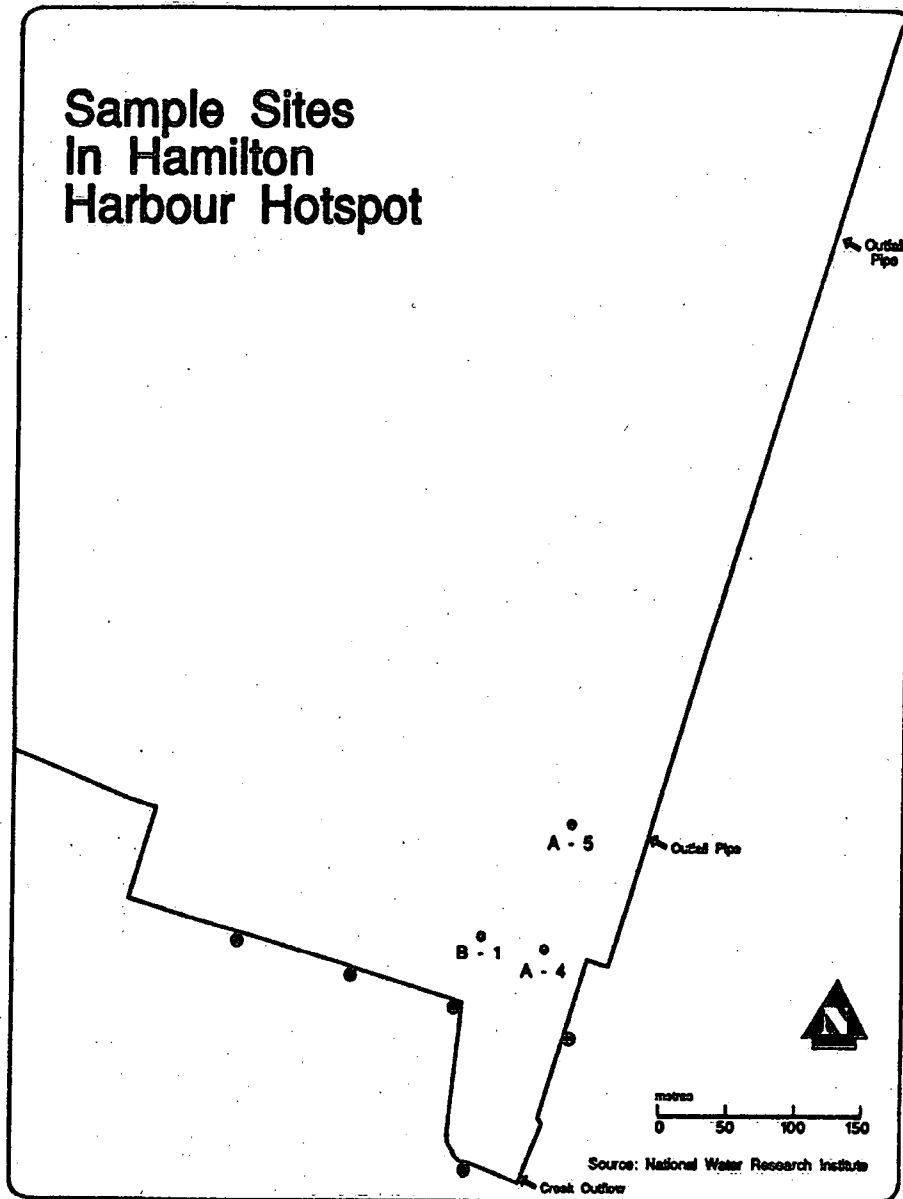
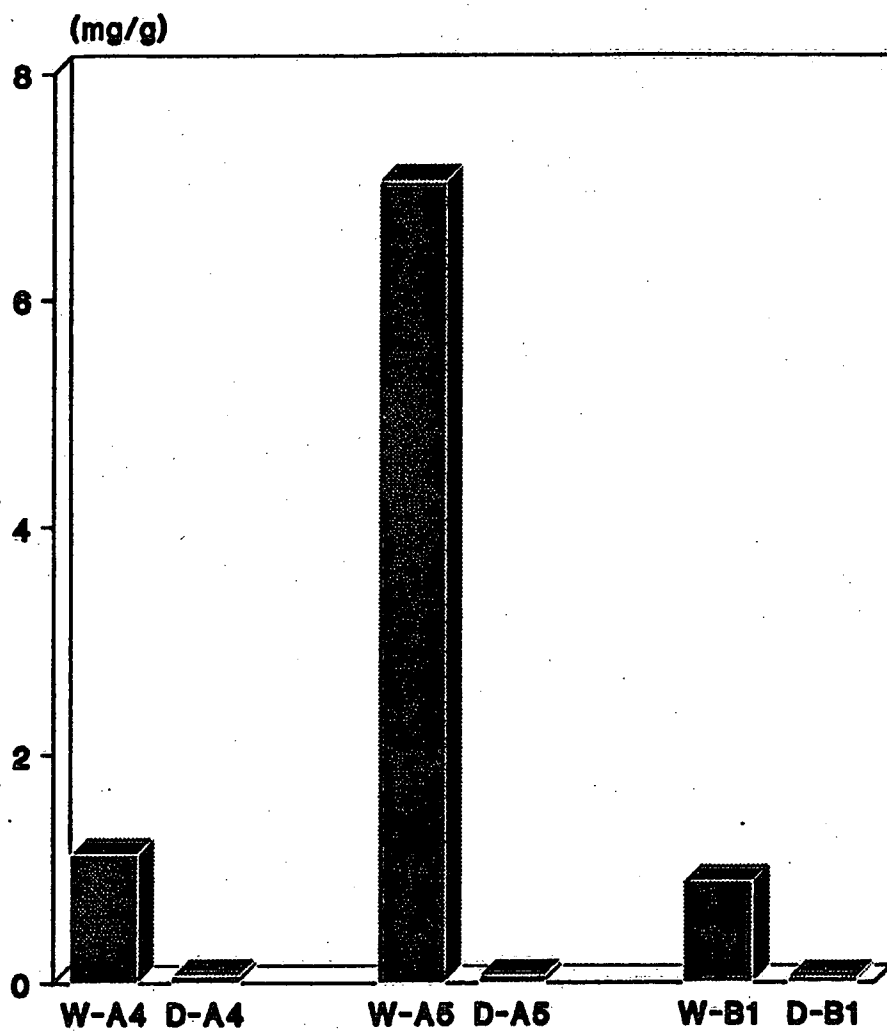


Figure 1. Sample sites in Hamilton Harbour hotspot.



W - Wet extraction
D - Freeze dried

Figure 2 The effect of freeze drying on naphthalene recovery.

Mean losses of naphthalene on freeze dried sediments from the three sites was 96%. Losses of pyrene were 42% and 14% for benzoperylene (Table 1). The trend in these decreasing losses is most readily explained by increasing molecular weight from the two fused rings of naphthalene through pyrene (four fused rings) to benzoperylene (six fused rings) with concomitant decreases in vapour pressure. Although the exposure time of the samples to freeze drying conditions is arguably excessive, the procedure used was typical of a busy laboratory processing large numbers of samples, and also gives a good indication of how extreme the losses may be.

Site	A5	
	Wet	F. Dried
Naphthalene	7041	61
Acenaphthylene	5	4
Acenaphthene	22	2
Fluorene	19	4
Phenanthrene	71	41
Anthracene	24	3
Fluoranthene	65	40
Pyrene	47	27
Benzo(a)anthracene	25	15
Chrysene	23	18
Benzo(b)fluoranthracene	41*	22
Benzo(k)fluoranthracene	NQ	10
Benzo(a)pyrene	22	13
Benzo(e)pyrene	13	11
Perylene	6	4
Indenopyrene	14	11
Dibenzoanthracene	4	3
Benzoperylene	14	12

* Sum of b and k isomers
 NQ Not quantified

Table 1 Concentrations of 18 selected PAHs ($\mu\text{g/g}$) at 10-12 cm in sediments from a coal tar contaminated site in Hamilton Harbour extracted 'wet' and after freeze drying.

Although high losses of several other PAHs were observed (acenaphthene 91%, anthracene 88%), the still larger losses of naphthalene may have much more significance to environmental assessments for the following reasons. The solubility of naphthalene at 31 $\mu\text{g/g}$ is more than ten times that of the other high loss PAHs. This higher solubility may be expected to exacerbate the acute toxicity of naphthalene to benthos exposed to pore water and at the sediment water interface. In Hamilton Harbour, The acute toxicity of the sediments was significantly correlated to the PAH concentration (Murphy et al., 1991). Furthermore, in coking operations, such as is found in Hamilton Harbour, naphthalene is by far the dominant PAH, accounting for fully 95% of the total PAH observed at site A5 (Table 1).

The inadvisability of freeze drying samples for PAH analysis has been addressed in the literature (John and Nickless, 1977), but the extreme potential for loss of naphthalene has not been emphasised as is evident from sample treatment practices commonly observed. Additional tests conducted in this laboratory but not reported here suggest that measurable but much lower losses of naphthalene and other PAHs occur when sediment samples are air dried at ambient laboratory temperatures.

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