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# PAH and Heavy Metal Pollution of the Sydney Estuary: Summary and Review of Studies to 1987

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## Canadian Technical Report of Hydrography and Ocean Sciences

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## Rapport technique canadien sur l'hydrographie et les sciences océaniques

Les rapports techniques contiennent des renseignements scientifiques et techniques qui constituent une contribution aux connaissances actuelles, mais qui ne sont pas normalement appropriés pour la publication dans un journal scientifique. Le sujet est généralement lié aux programmes et intérêts du service des Sciences et levés océaniques (SLO) du ministère des Pêches et des Océans.

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# PAH AND HEAVY METAL POLLUTION OF THE SYDNEY ESTUARY:

# SUMMARY AND REVIEW OF STUDIES TO 1987

by

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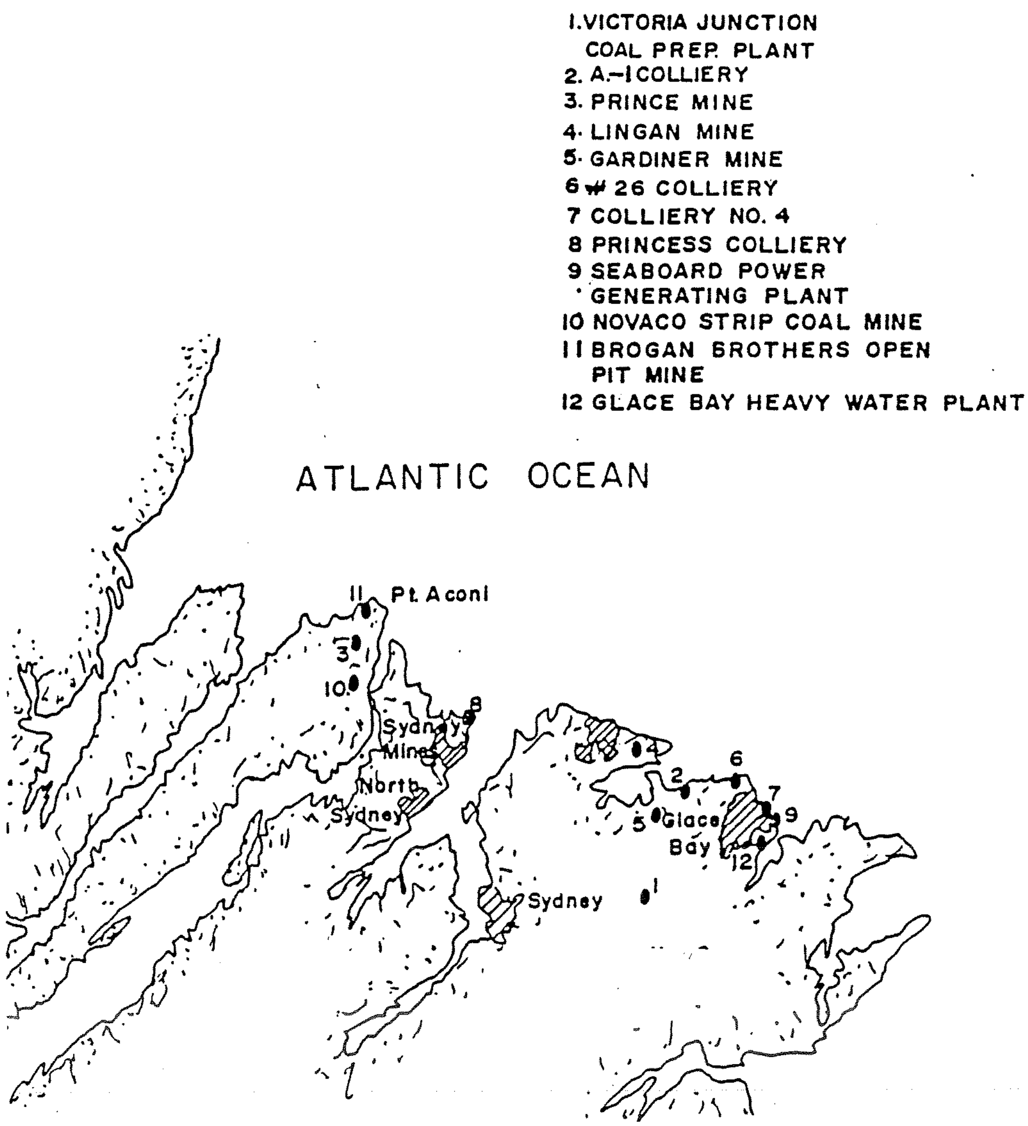


Location map showing relationship of Sydney steel operations relative to Sydney estuary. (From Matheson et al., 1983)

## ABSTRACT

Vandermeulen, J.H. 1989. PAH and heavy metal pollution of the Sydney Estuary: summary and review of studies to 1987. Can. Tech. Rep. Hydrogr. Ocean Sci. No. 108: ix + 48 pp.

The discovery of very high levels of ~~benzo(a)pyrene~~ PAH in lobsters (21,000 - 78,100 ng $g^{-1}$) from the Sydney estuary in 1980 led to initial surveys which indicated the Sysco coking facility and the nearby "tar pond" in Muggah Creek as the likely sources of hydrocarbon contamination. These facilities first began operations in 1899. A number of subsequent analytical surveys, focussing variously on sediments, waters, and biota gathered considerable data on bottom PAH and heavy metal contamination. PAH were present in all harbor sediments, and in many of the biota, especially in the South Arm. Little emphasis has been given to biological implications, except for some toxicity/mutagenicity assays which found toxic levels associated with some of the benthic sediments, and an unusual incidence of "red spots" on the underside of flounder taken from the South Arm.

Heavy metal pollution has received far less attention, although high to very high levels of cadmium, mercury, lead, and zinc have been found in bottom sediments throughout the estuary. Their sources undoubtedly are industrial, and very likely include the steel and coking operations. These data have come mainly from sediment studies carried out in support of dredging operations.

The summary impression of the data to 1987 is of widespread heavy metal and to a lesser extent PAH contamination of estuarine bottom sediments, with corresponding contamination of associated biota. Toxicity/mutagenicity assays of the Muggah Creek waters and sediments indicates the spread of mutagenic coal-tar derived contaminants into that part of the estuary. Another potential source of PAH and metal input into the estuary, by atmospheric transport from the coking operations, has not been evaluated. An integrated set of hydrographic with parallel analytical, physiological, and toxicological data is required for proper evaluation of the overall state of health of the estuarine system.

## RESUME

Vandermeulen, J.H. 1989. PAH and heavy metal pollution of the Sydney Estuary: summary and review of studies to 1987. Can. Tech. Rep. Hydrogr. Ocean Sci. No. 108: ix + 48 pp.

La découverte de concentration très élevées de ~~benzo(a)pyrène~~ PAH (21,000 - 78,100 ng.$g^{-1}$) chez les homards de l'estuaire de Sydney en 1980 a été à l'origine des enquêtes initiales qui ont incriminé la cokerie de Sysco et "l'étang de goudron" de Muggah Creek comme les sources vraisemblables de la contamination par les hydrocarbures. Ces installations sont entrées en service en 1899. Un certain nombre d'analyses ultérieures portant tantôt sur les sédiments, tantôt sur l'eau et tantôt sur la biotga ont permis de rassembler beaucoup de données sur la contamination du fond de l'estuaire par les HAP et les métaux lourds. Les HAP étaient présents dans tous les sédiments du port et dans de nombreux représants du biota, surtout dans le Bras Sud. On a très peu étudié les conséquences biologiques, sauf pour ce qui est de certains tests de toxicité/mutagenénicité qui ont révélé des concentrations toxiques dans certains sédiments de fond, et une incidence inhabituelle de "taches rouges" sur la partie ventrale de la plie capturée dans le Bras Sud.

La pollution par les métaux lourds a reçu beaucoup moins d'atttention, bien que des concentrations très élevées de cadmium, de mercure, de plomb et de zinc aient été observées dans les sédiments de fond dans tout l'estuaire. Il ne fait aucun doute que ces métaux lourds sont d'origine industrielles et il est très probable que les activités liées à l'acier et au coke soient en cause. Ces données proviennent principalement des études sur les sédiments réalisées en vue des opérations de dragage.

L'impression sommaire qui se dégage des données recueillies jusqu'en 1987, c'est que les sédiments du fond de l'estuaire sont fortement contaminés par les métaux lourds et, à un moindre degré, par les HAP, et que le biota associé à cette région est lui aussi contaminé. Des tests de toxicité/mutagénicité réalisés dans l'eau et les sédiments de Muggah Creek indiquent que l;es contaminants mutagènes provenant du goudron de houille se propagent dans cette partie de l'estuaire. Une autre source potentielle de HAP et de métaux lourds dans l'estuaire, à savoir le transport atmosphérique de polluant provenant des opérations de cokerie, n'a pas été évaluée. Un ensemble intégré de données hydrographiques, analytiques, physiologiques et toxicologiques est nécessaire pour permettre une évaluation appropriée de l'état de santé global de l'estuaire.

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## 1. INTRODUCTION

First reports of unexpected and very high levels of benzo(a)pyrene in lobsters taken from the Sydney estuary came in 1980. Mean hepatopancreatic levels (based on ten animals per sampling site) from the South Arm were 78,100 ng $g^{-1}$ wet weight (based on 12 PAH compounds), and from the South Bar were 21,000 ng $g^{-1}$. These concentrations were far in excess over estimated background levels in coastal lobsters, 3,000 ng $g^{-1}$. Subsequent environmental surveys of various potential PAH-sources in the area indicated the Sysco coking facility and the nearby "tar pond" in Muggah Creek as the likely sources of hydrocarbon contamination (Guilcher et al, 1982), with runoff and effluent from these apparently polluting the entire waters and biota of the greater Sydney estuary. The fact that benzo(a)pyrene was a known mutagen lent urgency to these findings. The fact that the tar pond had been in existence since the turn of the century, and had presumably contributed coal tar hydrocarbons all that time, dramatically lent magnitude to the problem.

A number of studies have since been done in the area, some in relation to the contamination problem per se, either in the tar pond, or more generally in the harbor, as well as a number of studies of harbor sediments in relation to dredging operations (viz. APPENDIX A).

Between 1981 and 1984 the federal departments of Fisheries and Oceans and of Environment Canada initiated initial surveys of the harbor and a number of land based sites, and firmly identified the Sydney "tar ponds" and specifically Coke Oven Brook as the sources of contamination (Matheson et al. 1983; Sirota et al. 1983, 1984). A parallel sampling program of the ambient air, carried out during 1981 and 1982, identified high PAH levels in the local atmosphere (Atwell et al. 1984). These were produced from a variety of coking operations, including dust from coal off-loading operations, and PAH-containing steam and smoke from the coking boilers.

In 1984, the firm Acres International Ltd, on behalf of EPS, carried out a survey of the steel plant and surrounding area, and of the tar pond, and prepared a list of recommendations to alleviate the problem (Acres, 1985). That study was restricted to the tar pond itself, and did not address the contamination problem downstream from the tar pond, either in the downstream portion of Muggah Creek or in the harbor waters generally.

Three surveys of harbor sediments have been carried out in support of dredging operations (Packman et al., unpublished report; OceanChem, 1984, 1986). In the course of this work, considerable data have been obtained on bottom PAH and heavy metal contamination, both from grab samples and from cores. All identified high to very high concentrations of PAH and of cadmium, copper, mercury, lead and zinc in harbor bottom sediments, especially from the South Arm.

Finally, two relatively small studies have addressed the problem of toxicity and potential mutagenicity of contaminated sediments (Odense et al., unpublished ms; Hutcheson et al. 1986; MacCubbin et al. 1986). Mutagenicity especially was frequently associated with riverine sediments containing high levels of PAH and/or mixtures of contaminants. Tay (personal communication) noted unusual incidence of red spots on the under- or ventral side of flounder taken from the South Arm.

Heavy metal pollution has received far less attention than PAHs, although high to very high levels of cadmium, mercury, lead, and zinc have been found in bottom sediments throughout the estuary. Their sources undoubtedly are industrial, and very likely include the steel and coking operations. These data have come mainly from sediment studies carried out in support of dredging operations.

## 2. LOCAL SETTING

### 2.1 Oceanography

The Sydney estuary is located on the north-east coast of Cape Breton Island, and receives saltwater from the outward flow from the Gulf of St. Lawrence. The estuary is Y-shaped, with two branches - the Northwest Arm and the South Arm. It is a relatively shallow inlet with maximum depths of 18 m in the outer harbor. A 13 m "bar" is located at the junction where the harbor splits into the Northwest and South Arms. The Northwest Arm and the South Arm are 6.5 and 13 kms long respectively, both with a maximum width of 1.6 km. Depths in the arms vary from 1 to 17 metres.

As an estuary, the system is primarily saline and is tidal in character. Freshwater input into the system is primarily by input from the Sydney River which enters at the head of the South Arm, and from small freshwater tributaries into the Northwest Arm. The influence of freshwater discharge on the hydrography of the whole system is thought to be minimal based on temperature and salinity measurements (Machell, 1972).

Physical oceanographic data for the system are scarce. The tides in the harbor are semi-diurnal with a mean amplitude of 0.9 m. Easton (1972) has recorded a seiche with a period of approximately 120 minutes, and amplitudes up to 0.6 m. Matheson et al. (1983) have reported on five dye-drift observations carried out in 1981. No other data or observations are available. The dye flow studies, carried out near the mouth of Muggah Creek between October 20 and 28 1981, have shown a consistent pattern of flow outwards into the South Arm (Figure 1). Dye was released from two locations - into Coke Oven Brook and to the surface of Muggah Creek - at different stages during the tidal cycle. The dye patch entered the South Arm as a single plume, and remained at or near the surface, moving thence into the harbor proper towards the mouth of the harbor. In one release, just after high tide

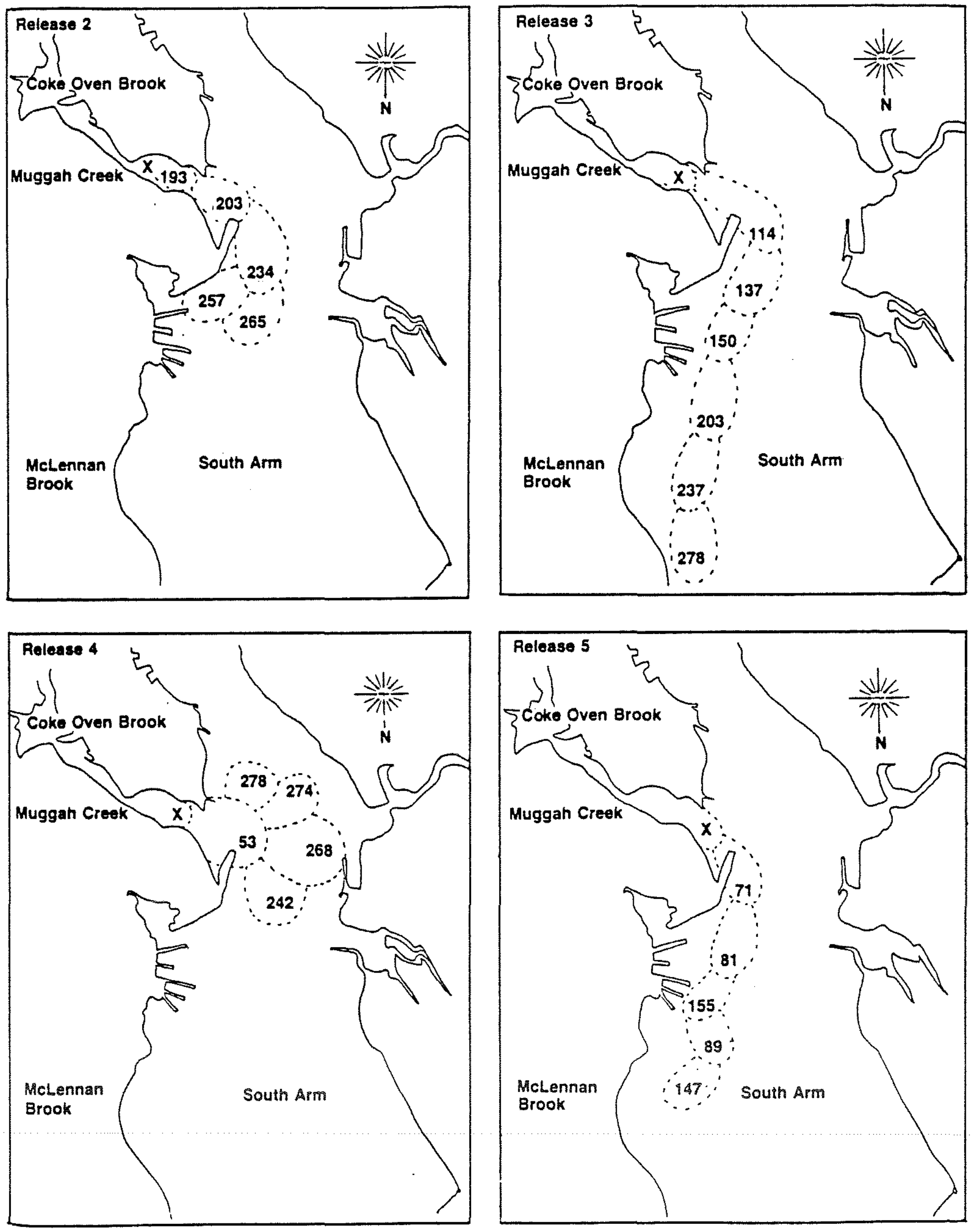


Figure 1. Flow patterns of dye (rhodamine w.t.) released at different times from Muggah Creek and Coke Oven Brook. (From Matheson et al., 1983)

with a north-east wind, the dye patch was observed to move into and cover the central area of the harbor before eventually moving toward the harbor mouth and dissipating.

The experimental results indicated that the dye-tracer was influenced significantly by wind, the latter frequently overriding tidal flow. The dye-tracer moved most rapidly and traveled the greatest distance toward the mouth of the harbor when it was released during ebb, with the wind from the southwest. Conversely, during conditions of ebb and moderate northeast winds, the dye patch moved in the opposite direction from the tide, and in the same direction as the wind.

In most cases, dye was found no deeper than 1.5 m down in the water column. Greater mixing and dispersion occurred on the rising tide, presumably due to more active turbulent mixing of incoming tidally-drive saltwater with outgoing Muggah Creek drainage water.

From these limited results, it was concluded that surface circulation of the harbor was primarily influenced by wind when wind speeds exceeded 10 km $h^{-1}$, and by tidal flow alone at lower wind speeds. Outflowing water from Muggah Creek would seem to remain relatively unmixed and remain the near surface of the South Arm water column, except with the incoming tide.

## 2.2 Sedimentology

The sedimentology of the estuary has been reviewed by OceanChem (1986) (Figure 2a-d). The South Arm of the system is characterized by fine sediments. For example, the silt/clay fraction formed 80% or more of the sediment in the Sydney River and the South Arm (OceanChem, 1986). It is suggested that much of these fines are derived from three sources - from the Sydney River itself, from particulates from Muggah Creek, and from shoreline slag piles onshore of Muggah Creek.

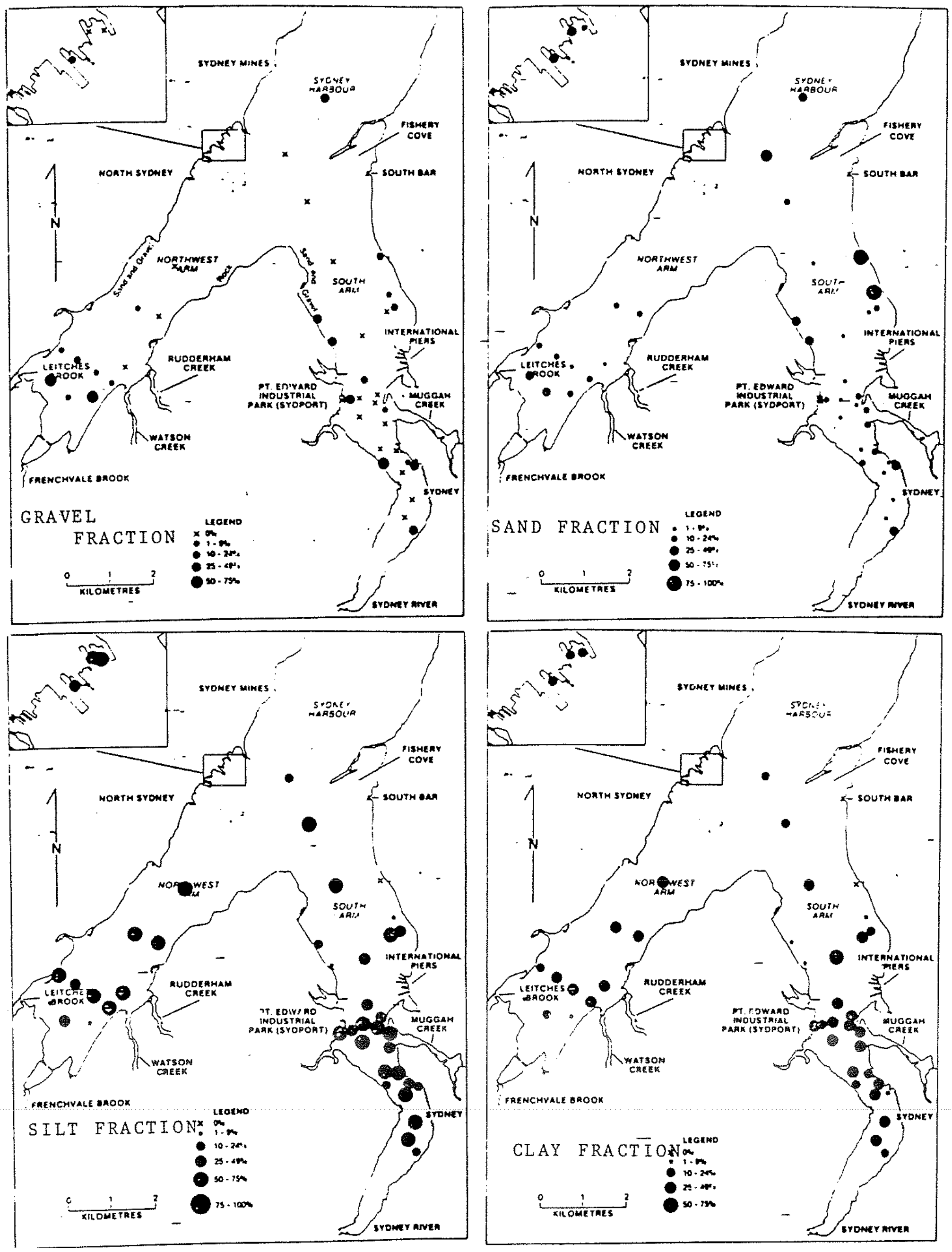


Figure 2. Sediment grain size data for Sydney Harbor (from Packman et al (unpub. rept).

In contrast, the North West Arm and the Outer Harbor are thought to have little sedimentological input from the South Arm (OceanChem, 1986), because these lack the high fines percentage. OceanChem indeed suggests that much of the South Arm material is a) retained in the South Arm, b) gradually accumulates at the South Bar, and c) if it does become directed into the North West Arm, it becomes diluted by "cleaner" sediments.

Sediments in the estuary are generally fairly rich in organic carbon (Figure 3), especially in the South Arm and in the most interior part of the North West Arm where total organic carbon forms 4 to 7 percent of the sediments.

## 2.3 Anthropogenic Inputs

Man's presence in and impact on the estuary is fairly limited, both in terms of population and industrialization. The cities of Sydney, Sydney Mines and North Sydney form the urban activity of the area, with the bulk of the population located in Sydney (1981 population 29,444). Sydney harbor serves many activities - fish processing, trans-shipment of petroleum products, general cargo shipment, ship repair, and trans-shipment of coal, iron-ore and steel. The Cape Breton terminal of the ferry to Newfoundland is located in North Sydney. Industrial activity is centered mainly in the Sysco operations involving coal-coking and steel manufacture.

Historically, pollution of the estuary has involved a mix of wastes from these various point-sources. Domestic pollution consists primarily of untreated waste from the city of Sydney. Industrial pollution comes mainly from the Sysco steel operations and from the coking plant. Commercial pollution is a minor factor. Chemically, contaminants range from heavy metals, PCBs and DDT, ammonia, phenols, cyanide, phosphate, and coal tar derivatives (Hildebrand, 1982).

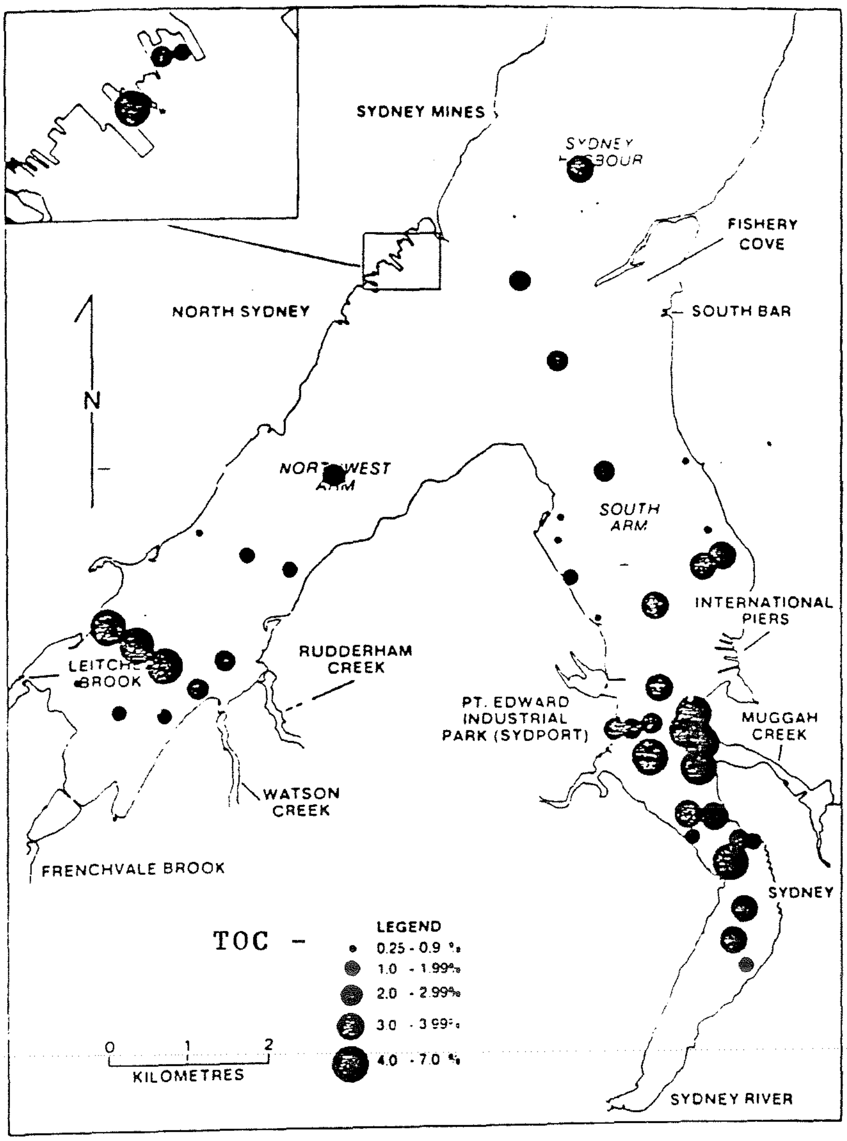


Figure 3. Total organic carbon concentrations for Sydney Harbor sediments (from Packman et al., unpublished report).

## 2.4 Biological Resources

### 2.4.1 Fin- and shell-fish

A good evaluation of the biological resources of the harbor is not available, for two reasons. The harbor and estuary itself represents only a limited fishery resource and no biological surveys have been done in the area. And fisheries statistics for the area are at best sketchy.

Mackerel and cod both migrate offshore, and have been reported in the harbor. EPS trawls (Packman et al., unpub. rept) carried out in the harbor system in August 1983 captured winter flounder (Pseudopleuronectes americanus, hake (Urophycis tenuis), and cunner (Tautoglobrus acesperus). Flounder in the EPS trawls from the South Arm were a mixed age group, while catches from the Northwest Arm and the Outer Harbor reflected a mature population. Hake were mostly young-of-the-year.

Smelt-fishing is a limited activity, mainly recreational, and primarily in the Northwest Arm where a reportedly large smelt population migrates through the Arm and up into the creeks and tributaries (OceanChem 1984). Similarly salmon are a small but significant sport fishery, again mainly in the Northwest Arm. Sport fishing for mackerel and herring is also important, especially off wharves in Sydney, North Sydney and Sydney Mines.

Groundfish fishery is a viable activity, mostly by handlining, around the mouth of the estuary. Major species caught are cod.

OceanChem (1984) reports a commercial fishery for lobsters within Sydney harbor employing 39 fishermen, each with approximately 275 traps. The South Arm has been banned to lobster fishing because of PAH contamination. Very little lobstering is done in the Northwest Arm. Lobstering activity on the south shore takes place between Pt. Edward and Low Point, on the north shore from Northwest Arm to Sydney Mines and Alder Point. There is reportedly a good lobstering ground in the outer harbor.

There is a mollusc and crustacea (shrimp) industry ($500-800,000, for 1980), but it is unclear whether this is for the estuary or for product taken from outside the harbor. Sydney is a major site for fish stock landings, circa 20-40,000 metric ton, all of it from offshore catches. Currently all of Sydney estuary is closed to shellfish harvesting because of PAH contamination.

### 2.4.2 Bottom communities

Very little information exists on benthic communities for the system. Two benthic surveys, one in 1979 and one in 1983, provide some data (Wendland, 1979; Packman et al, unpub. rept; also Hildebrand, 1982). The Northwest Arm seems to contain a thriving and diverse benthic community. In contrast, the South Arm benthos shows clear impact of tar pond effluent, with polychaetes and sea anemones the dominant species. Benthos near Muggah Creek were in very low numbers, increasing in numbers with distance from Muggah Creek. Interestingly, Wendland (1979) reports evidence in the South Arm of greater pollutant impact on the eastern side than on the western side. Oceanchem (1984) speculates that this may reflect three factors - the effluent dispersion pattern for Muggah Creek (viz. dye studies, Matheson et al 1983; also this section 2.2 Oceanography), the particular sediment geochemistry (viz. Pack et al, unpub report), and potential contaminated surface runoff from the industrialized eastern shore of the South Arm.

## 3. COAL-TAR AS A CONTAMINANT

Coal tar is a by-product of the "coking" of bituminous coal, the production of coke necessary for steel production in blast furnaces. It is a formed when coal is heated and decomposed anaerobically at temperatures from 900 to 1200 $^{o}$C. It is a primary distillate, with high to very high concentrations of aromatic and polycyclic aromatic hydrocarbons (PAH). Some coal tar has been known to consist of up to 48.5 % PAH. Lao et al (1975) have analyzed for and identified 60 distinct PAH's in coke oven emissions. Creosote, a highly toxic hydrocarbon-based wood preservative, is a coal tar derivative.

Coking of coal is considered a major contributor of PAH pollution into the environment, either directly into aquatic sources by dissolution or via atmospheric emission. The U.S. National Academy of Sciences (1972) estimates that coal coking releases circa 0.2 x $10^6$ kg benzo(a)pyrene (BaP) into the environment annually, i.e. approximately 1.8 g BaP per ton coal coked.

Coal tar is similar in composition to synthetic coal and shale fuels. Toxicologically their impact lies in their toxicity to living organisms, and in their tumorigenic and carcinogenic effects. Many of the PAH identified in coal tar and coal tar effluent are known to cause tumors and elicit carcinogenesis (e.g. Ames et al., 1975; McCann et al., 1975; Guerin et al., 1978). Their accidental introduction into aquatic systems (rivers, lakes, estuaries) therefore has the potential of permanently impacting on fish stocks through causing tumors and lesions.

## 4. MUGGAH CREEK AND THE TAR-PONDS

The source of the harbor PAH contamination has now been directly traced to the "tar ponds" and specifically to Coke Oven Brook effluent (Packman et al., unpub. rept; Matheson et al., 1983) emptying into Muggah Creek. Muggah Creek is partly tidal, and reportedly has an estimated drainage area of from 10 to more than 30 million gallons per day, depending on the time of year and on other hydrologic factors (Hildebrand, 1982).

While the actual starting date of the input of coal tar products

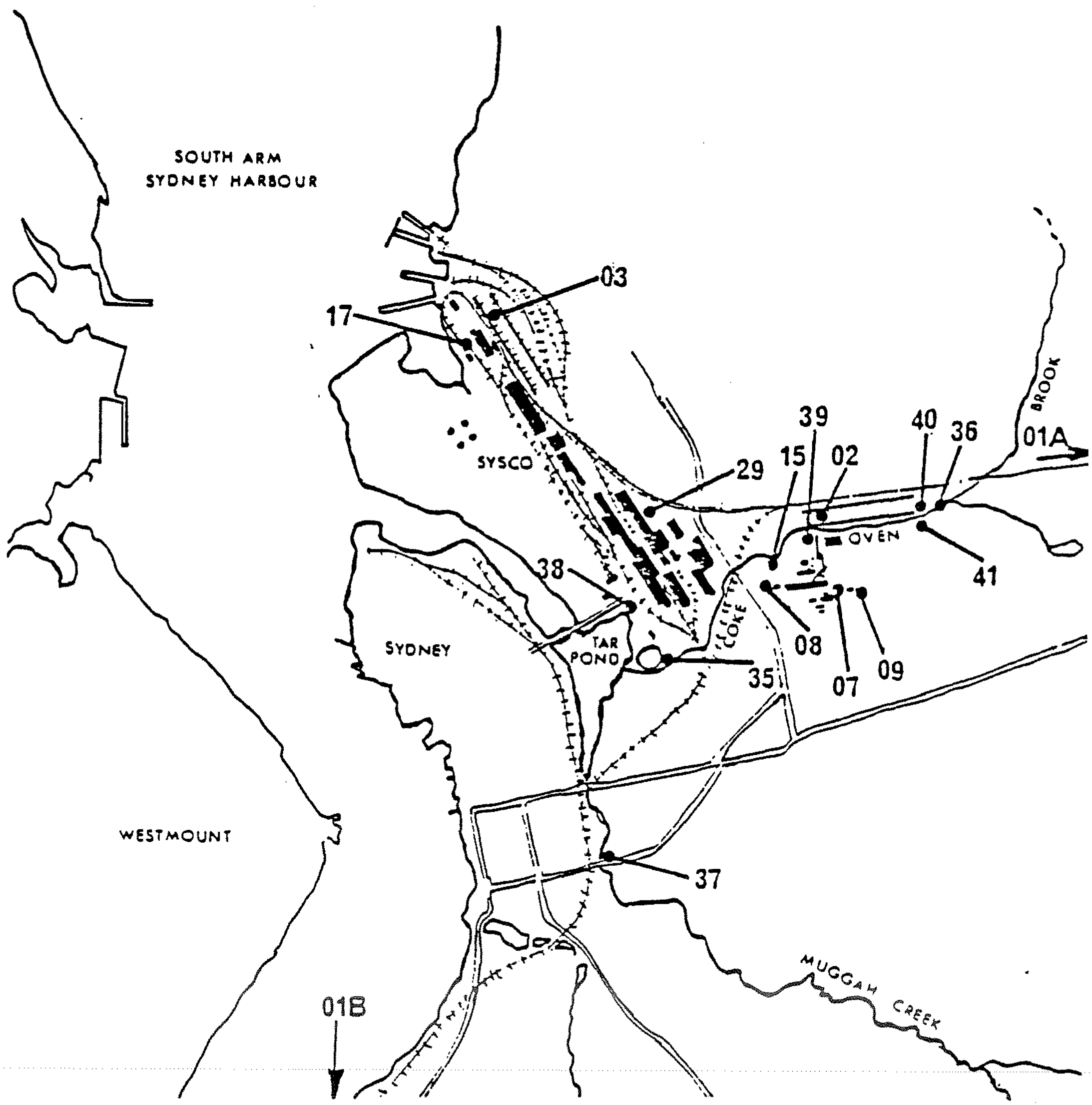


Figure 4. Detail of Sysco steel facilities in relation to Muggah Creek and the South Arm of Sydney Harbor. (From Matheson et al., 1983)

into the Sydney estuary is not known with certainty, it presumably parallels the start-up of the Sydney steel manufacturing operations which began in 1899. Effluents from the operation together with surface and groundwater from the immediate area, including coal storage, were allowed to flow via Coke Oven Brook into Muggah Creek (Figure 4) which practice was then continued to the day. The principal source of the contaminants was and remains the coking operation at the Sysco facility. Further contributions probably came from a Dominion Tar and Chemical Plant (since discontinued and dismantled in 1963), from two tar storage ponds, from the Coke Oven Chemical Plant (Sysco) and from other Sysco operations.

It is likely that all soil underlying the plant and constituting the bed of Coke Oven Brook has been contaminated for years to decades. This has been undoubtedly contributed to by general uncontrolled burial and disposal practices, including the burying of tar wastes from time to time in any available open excavation (Acres, 1984).

Also, the surficial deposits of the steel plant can be considered relatively porous to hydrocarbons, consisting of a 3 to 5 m continuous layer of silty sand-gravel-cobble material, and are therefore highly vulnerable to cross-contamination. General runoff through these sediments undoubtedly contributed coal-tar PAH and metals to the general pollution in Coke Oven Brook.

Packman et al. (unpubl. rept) report flow rates for the various potential sources, ranging between thirteen to twenty million litres per day, and estimated a combined contribution to Sydney Harbor of up to one metric tonne PAH per year via Coke Oven Brook.

With the passage of time, the outflow area in Muggah Creek expanded to eventually form the "tar pond", a body of coal tar sludge covering several acres in area and in places over 11 feet deep. The tar-pond is physically divided into two ponds, the south pond (upstream from Ferry Street) and the north pond (downstream from Ferry Street). Soil borings in the south pond have shown up to 9 feet of coal wastes and tar residue overlying the original silt creek bed. Maximum thickness was found near the center of the south pond, at 11.6 ft. The total volume of coal-tar and coke contaminated sediments in the south pond is estimated to be 350,000 $yd^3$. Contaminated sediments in the north pond varied in thickness from 14.5 ft, in the area just upstream from the mouth, to 2.5 - 4.5 ft, at the mouth itself. Total volume of coal tar contaminated sediments in the north tar pond has been estimated to be 650,000 $yd^3$.

In total, the "tar pond" is estimated to contain 1,000,000 $yd^3$ (ca. 500,000 tonnes dry weight) of contaminants. Most of this consists of coal and coke particulates, ranging in size from less than 0.1mm up to 2 cm in diameter. The bulk of the material is 1 mm or less in diameter.

Over 40 hydrocarbons have been individually identified in the contaminated sediments (Matheson et al. 1983). These include the sixteen PAHs which are listed on the US Environmental Protection Agencies List of Priority Chemicals. In addition, a wide range of heavy metals were identified in the tar pond material. Also identified was the compound di-n-butylphthalate which is not associated with coal or coal tar, but is a widely used plasticizer and is characteristically identified in industrial effluents.

Estimates of the amount of PAH in the tar pond vary widely, and have been calculated at 600 ug $g^{-1}$ to 30,000 ug $g^{-1}$ dry weight, with a representative average concentration of 4,600 ug $g^{-1}$ dry weight in surface samples and 6,900 ug $g^{-1}$ dry weight in subsurface samples. Using the figure of 500,000 tonnes total dry weight of sediment, there may be as much as 3.5 million kg of PAHs stored in the tar ponds.

Heavy metal content in tarpond samples is high, representing a very wide range of metals from aluminum (3.8-7.4 mg $gm^{-1}$ wet weight) to zinc (0.1-0.56 mg $gm^{-1}$ wet weight), including all the common toxic elements (Matheson et al. 1983).

## 5. WATER-BORNE PAH & METAL INPUT TO HARBOR WATERS

### 5.1 PAH Input

There are a variety of PAH and other hydrocarbon sources, including from general urban runoff, and from the ferry terminal in the Northwest Arm. Undoubtedly the bulk of PAH input, however, is from the Sysco steel and coking operations, principally from the tar-pond. Input of tar-pond material into the Sydney harbor/estuary is by a mix of freshwater flow (circa 18 to 22 $ft^3$ $s^{-1}$ at the mouth of Muggah Creek from several small streams and city sewers and groundwater) and by tidal flushing and seiching. These are thought to be the major processes causing turbulent mixing in Muggah Creek (Acres, 1985).

PAH and other tarpond constituents enter Muggah Creek in both soluble and particulate form. Based on Coke Oven Brook outflow measurements on two sampling dates, it would seem that between 100 and 200 g PAH flow into Muggah Creek per tidal cycle. This extrapolates to an annual output of circa 100 kg $yr^{-1}$. Other mass balance calculations place the net release of PAH into Muggah Creek at approximately 81 kg $yr^{-1}$.

Actual output of PAH into the downstream Sydney harbor waters has varied over the years. Matheson et al (1983) estimated a net PAH release for 1981 from Muggah Creek of 3,500 kg $yr^{-1}$. Subsequently Acres (1985) estimated a net release of approximately 106 kg $yr^{-1}$. It is possible that in preceding years the outflow was even higher. The difference between current and past releases can be attributed in part to shutting down of coking operations.

Analyses of water samples from creek outflow during two sampling dates (May 31 and June 22, 1984) have provided some insight into PAH transport

Table 1

PAH release into Sydney Harbor from Muggah Creek, per tidal cycle (measured) and per annum (calculated) (Acres, 1985).

| PAH | Transport ($g$ tidal cycle$^{-1}$) May 31 | Transport ($g$ tidal cycle$^{-1}$) June 22 | Transport ($kg\ yr^{-1}$) |
|---|---|---|---|
| acenaphthene | 22 | 3 | 8 |
| acenaphthalene | NM | 7 | |
| fluorene | 35 | 11 | 15 |
| phenanthrene | 56 | 21 | 26 |
| anthracene | 10 | 6 | 6 |
| fluoranthene | 55 | 27 | 28 |
| pyrene | 24 | 13 | 13 |
| benzo(a)anthracene | 7 | 5 | 4 |
| chrysene | 8 | 3 | 4 |
| benzo(b)fluoranthene | 0.4 | 3 | 1 |
| benzo(k)fluoranthene | 0.4 | 3 | 1 |
| benzo(e)pyrene | -0.3 | 1 | u.c. |
| benzo(a)pyrene | -0.2 | 2 | u.c. |
| indeno-pyrene | N.D. | -1 | u.c. |
| benzo(ghi)perylene | N.D. | 1 | u.c. |
| Total PAH | 217 | 105 | 106 |

NM = not measured; N.D. = not detected; u.c.=uncertain, very small value which is not reliable and may be either positive or negative.

into the harbor waters (Table 1). Not unexpectedly, the PAH output from the tar pond appears heavily influenced by tidal variation. Highest output was on May 31, when tidal range was circa 1.75 ft higher than on the other sampling date, June 22.

Compositionally, the material contains the full suite of PAH from acenapthene to benzo(ghi)perylene. The bulk of PAH was represented by acenapthene, fluorene, phenanthrene, fluoranthene and pyrene.

## 5.2 Input of Metals

No data are available either on the amounts of metals contained in the tar pond, or on the efflux from the tarpond.

## 6. ATMOSPHERIC INPUT OF PAH AND METALS INTO THE ESTUARY

### 6.1 PAH

None of the studies todate have considered the potential input of PAH to the harbor/estuary via atmospheric transport. Hildebrand (1982) has reported on a variety of emission sources, but primarily from an air pollution/human health point of view (Table 2). Atwell et al. (1984) also has focussed on ambient air PAH contamination, primarily as it results from the Sysco operations. Neither gives estimates of PAH and/or contaminant inputs to the estuary.

Hildebrand (1982) has identified particulate emission to the atmosphere as a potential significant source of contaminants (ca. 28,000 tonnes $yr^{-1}$). Of this total, 76% of the particulate material emanates from the open hearth furnaces and 19% from the blast furnaces. No distinction was made in this report on the basis of PAH specifically, although the author notes that the coke ovens may have been emitting elevated levels of atmospheric PAHs.

Table 2

Major contaminant emissions to atmosphere in Sydney area. (From Hildebrand, 1982).

| Source | contaminant | emission |
|---|---|---|
| Sysco | $SO_2$ | 3,360-10,862 tonnes (1973-78) |
| | particulates | 18,500 tonnes $yr^{-1}$ |
| domestic and commercial heating | $SO_2$ | 3,000 tonnes $yr^{-1}$ |
| | particulates | 400 tonnes $yr^{-1}$ |
| thermal generation plants | | |
| Seaboard plant | $SO_2$ | 16,824 tonnes, 1980 |
| | particulates | 4,263 tonnes, 1980 |
| | $NO_x$ | 8,716 tonnes, 1980 |
| Lingan plant | $SO_2$ | 24,323 tonnes, 1980 |
| | particulates | 646 tonnes, 1980 |
| | $NO_x$ | 5,605 tonnes, 1980 |
| coal transportation | particulates | 4,200 tonnes $yr^{-1}$ |

More detailed data on atmospheric PAH input and transport are contained in the subsequent report by Atwell (1984). PAH emissions from coke oven operation can originate from a variety of stages in the coking process - coal offloading and filling of furnace, coking cycle itself, oven emptying, coke cooling, and underfiring.

Estimated emissions for the Sydney coke ovens (c.f.) put circa 3770 PAH into the air from coking operations. Actual measured atmospheric concentrations of PAH and BaP for the city of Sydney are difficult to compare with these estimates, but they are considerable (Table 3). While a correlation between atmospheric PAH loading and wind speed was not clear, highest PAH and BaP values were obtained downwind of the Sysco operations at higher wind speeds. For example, for the Frederick Street sampling location, 201.56 ng $m^{-3}$ was recorded when the wind was 100% from the direction of the coke ovens at 19 km $hr^{-1}$.

Table 3

Ambient PAH emissions determined for three sampling locations in Sydney, N.S. (From Atwell et al., 1984)

| Air sampling station | total particulate PAH (ng $m^{-3}$) | total BaP (ng $m^{-3}$) |
|---|---|---|
| County Jail | 0.36-622.4 | 0.02-36.42 |
| Frederick Street | 0.69-201.56 | 0.06-21.14 |
| St. Rita's Hospital | 0.09-23.70 | n.d. - 1.98 |
| Average | | 1.9 |

C.f. Based on US EPA data for uncontrolled metallurgical coke manufacturing operations, and that 1.4 tonnes of coal are required to produce 1 tonne coke. kg $day^{-1}$

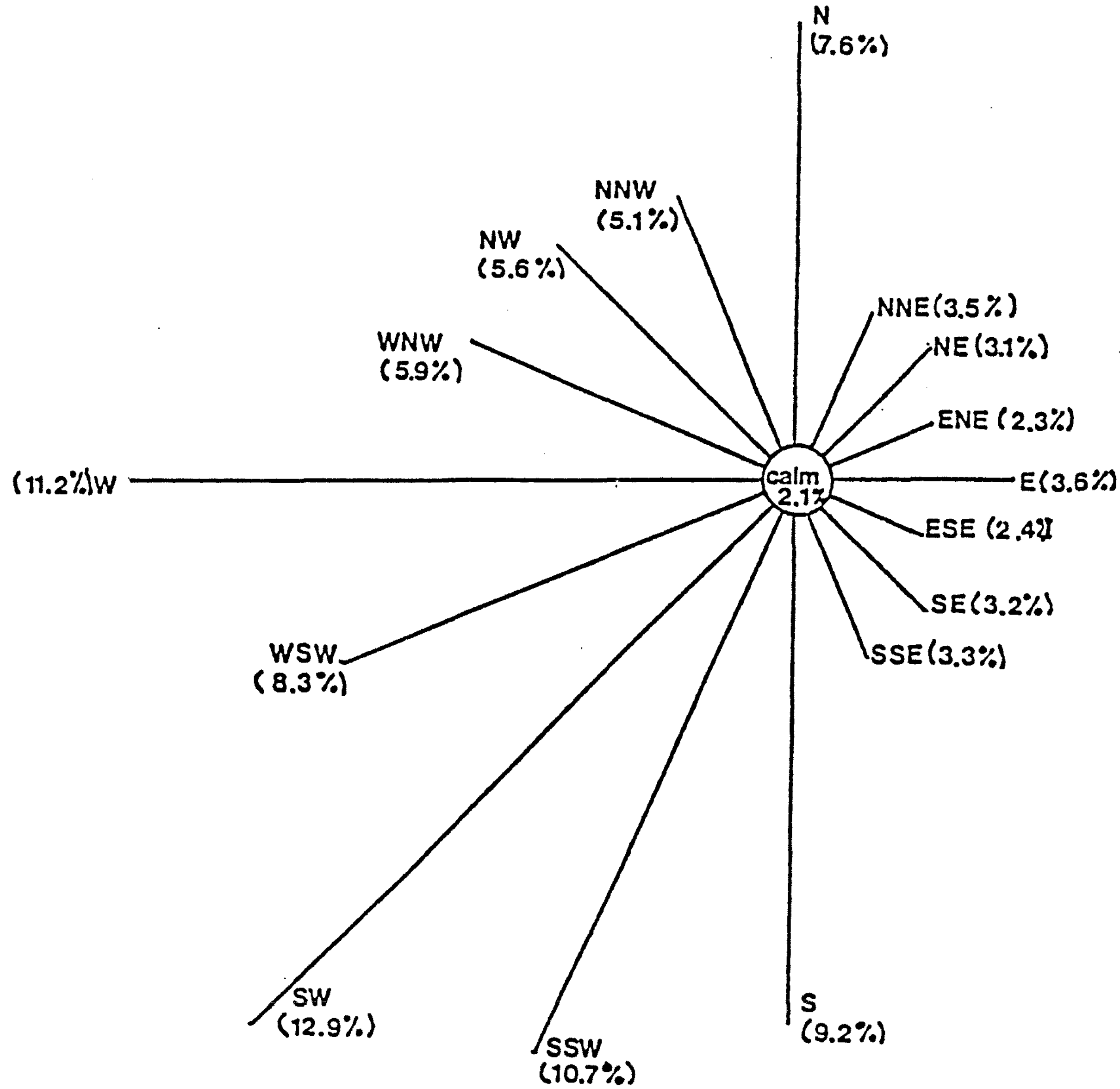


Figure 5. Wind rose for Sydney Airport, based on 1955 to 1980 data. (From Atwell et al., 1984).

The risk of the Sydney estuary, relative to Sydney and the Sysco PAH source, is very much wind-direction dependent. The wind rose for Sydney Airport (Figure 5) indicates a likelihood of less than 21% (of the time) of prevailing north-easterly to south-easterly winds blowing toward the estuary.

Nonetheless, this route represents another potential source of PAH and metal input into the system the magnitude or rate of which to date has not been measured or evaluated.

## 6.2 Atmospheric Metal Inputs

No data are available on transport/input of heavy metals into the Sydney estuary.

## 7. COAL-TAR AND METAL POLLUTION IN SYDNEY HARBOR AND ESTUARY

Environmental work todate in the Sydney Harbor-estuary proper has been restricted principally to determinations of PAH and metal concentrations in 1) sediments (Packman et al., unpub. rept; Matheson et al, 1983; Sirota et al., 1983; Ocean Chem, 1986; MacKnight and Sirota, 1986), and 2) lobster and mussel tissues (Sirota et al., 1983, 1984; Uthe and Musial, In Press) (also see APPENDIX C). Much of the sediment-contaminant data has come from sediment analyses in support of dredging operations and consequently lack correlation with either associated biota or the overlying water column. Some limited work exists on the mutagenic/tumorigenic potential in sediments and mussels, primarily from the South Arm (Odense, 1982; Hutcheson et al., 1986; Odense et al., In Press; MacCubbin et al., 1986).

Most work has been done in the South Arm, immediately downstream of the tar pond. Packman et al. (unpub), Matheson et al. (1983) and OceanChem (1986) provide data on the larger estuary.

## 7.1 Water Contamination

No data exist for PAH or heavy metal contamination for the harbor waters, downstream from the tar pond. This is a surprising and serious gap in the data, given the potential magnitude and seriousness of the problem.

## 7.2 Sediment Contamination

### 7.2.1 PAH

Intertidal sediments downstream of the tarpond outfall have been shown to contain a wide range of contaminants - PAH, organic synthetics, metals - several at high to very high concentrations (Table 4). Total PAH levels compare to the very high concentrations found in other studies of river sediments near heavily industrialized centers (for ex. Elizabeth River, Virginia) (Hargis et al., 1984).

Table 4

Contaminants in intertidal sediments of Muggah Creek, downstream from the tarponds. (Data from Hutcheson et al., 1986)

| Contaminant | concentration ($ng\ g^{-1}$ dry weight) #1 | #11 | #20 |
|---|---|---|---|
| total PAH | 5.5 | 142 | 911 |
| BaP | 0.59 | 12 | 68 |
| PCB | 20 | 1,730 | 52,000 |
| total chlorinated pesticides | +(1) | ++ | ++++ |
| total chlorophenols | nd | 307 | 18.6 |
| total phthalate esters | 80 | 7,100 | 6,080 |

The presence of PCB, chlorophenols and phthalate esters was unexpected for what was thought to be a single-species (PAH) pollution source. PCB is now thought to be coming from transformers used at Sysco. Phthalate esters are a common contaminant, they derive from plasticizers, and may originate from various industrial uses in the area. The chlorophenols apparently derive from wood preservatives and pesticides and may arise from various forestry related activities, as well as from industrial sources around Sydney.

Bottom sediments appear to be widely contaminated, over a range of concentrations. Packman et al (unpubl. EPS rept) analyzed 50 bottom sediment

Table 5

Concentrations of polynuclear aromatic hydrocarbons (total PAH) in sediments from South Arm, Northwest Arm and downstream Sydney Harbor.

| | Station* | Packman et al. (unpubl. data) mg g-1 dry wt | Matheson et al. 1983 mg g-1 dry wt |
|---|---|---|---|
| Sydney R. | 36-43 | 29.7 - 323.0 | 16.0 - 79.0 |
| Central S. Arm | 26-35 | 41.6 - 2,101.0 | 41.0 - 2,800.0 |
| Outer S. Arm | 18-25 | 8.5 - 179.32 | 13.0 - 750.0 |
| NW Arm | 8-17 | 0.67 - 18.99 | 2.5 - 8.2 |
| Outer Harbor | 1-7 | 12.93 - 18.04 | 0.13 - 10.0 |

* Matheson et al 1983 stations

samples for PAH and heavy metals, as well sediment particle size distribution. Their results, summarized in Table 5, indicated high to very high PAH levels in the South Arm, with the highest values clustered principally around the mouth of Muggah Creek. However, even bottom sediments from the outer harbor contained detectable levels of PAH and heavy metals.

Packman et al's values (Table 5) are similar to those reported by Matheson et al. (1983) and Sirota et al. (1983) for samples from a grid of 44 sediment stations, including from the South and Northwest Arms and the immediate downstream portion of Sydney Harbor (Figure 6). Samples were obtained either by grab (Ekman sampler) or as cores. Hydrocarbon (total PAH) concentrations in harbor sediments varied considerably, but grouped into four distinct clusters, with highest values in sediments taken from the South Arm directly below the mouth of Muggah Creek, and lowest values taken well downstream in Sydney Harbor.

Bottom PAH concentrations may possibly be higher than reported here. Matheson et al. (1983) have noted that in some comparative analyses between cores and grab samples, PAH concentrations in aliquots from grab samples were higher, by from 15 to 38%, than aliquots taken from the top 3 cms of sediment

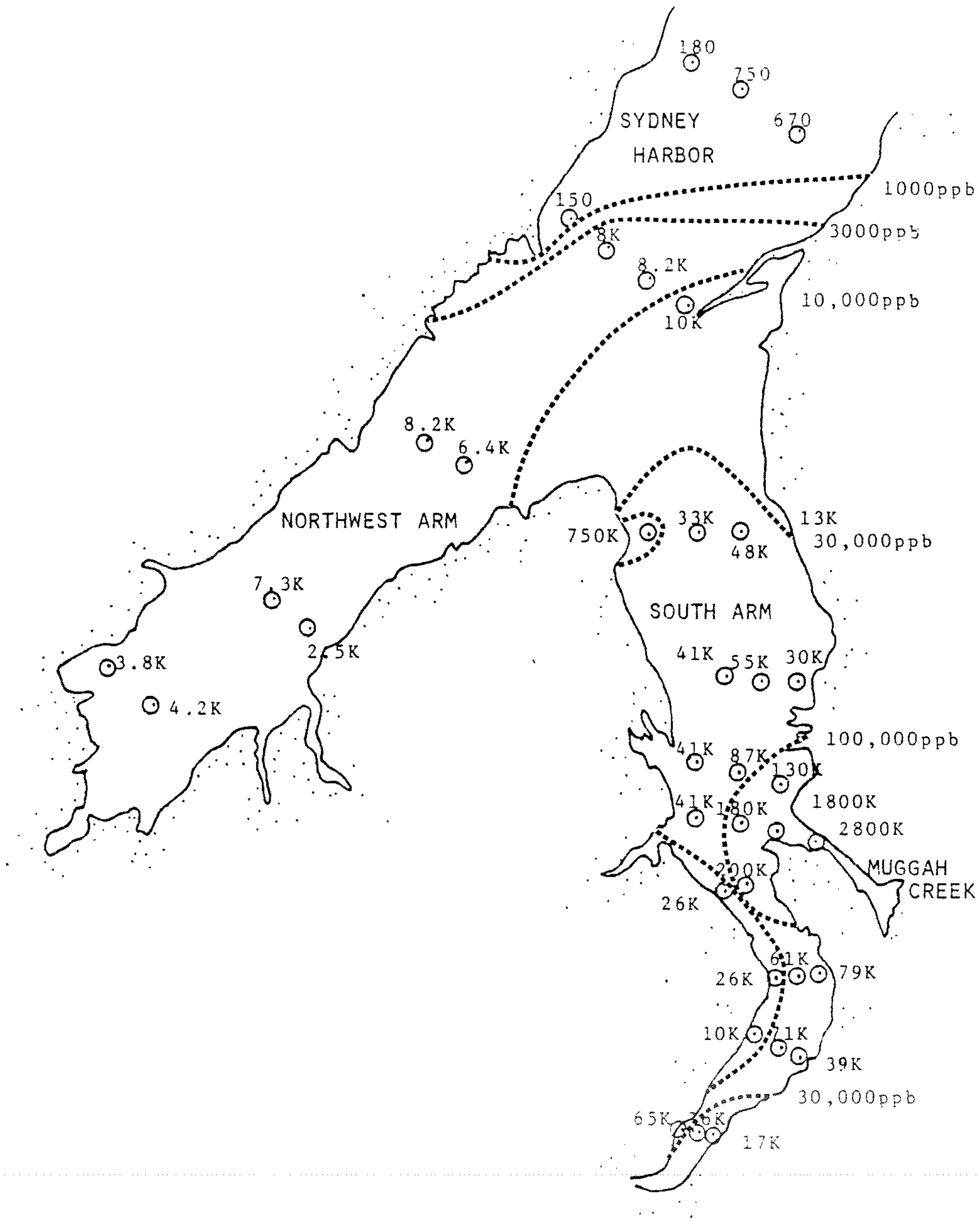


Figure 6. PAH concentration contours in bottom sediments from Sydney Harbor (redrawn from Matheson et al. 1983)

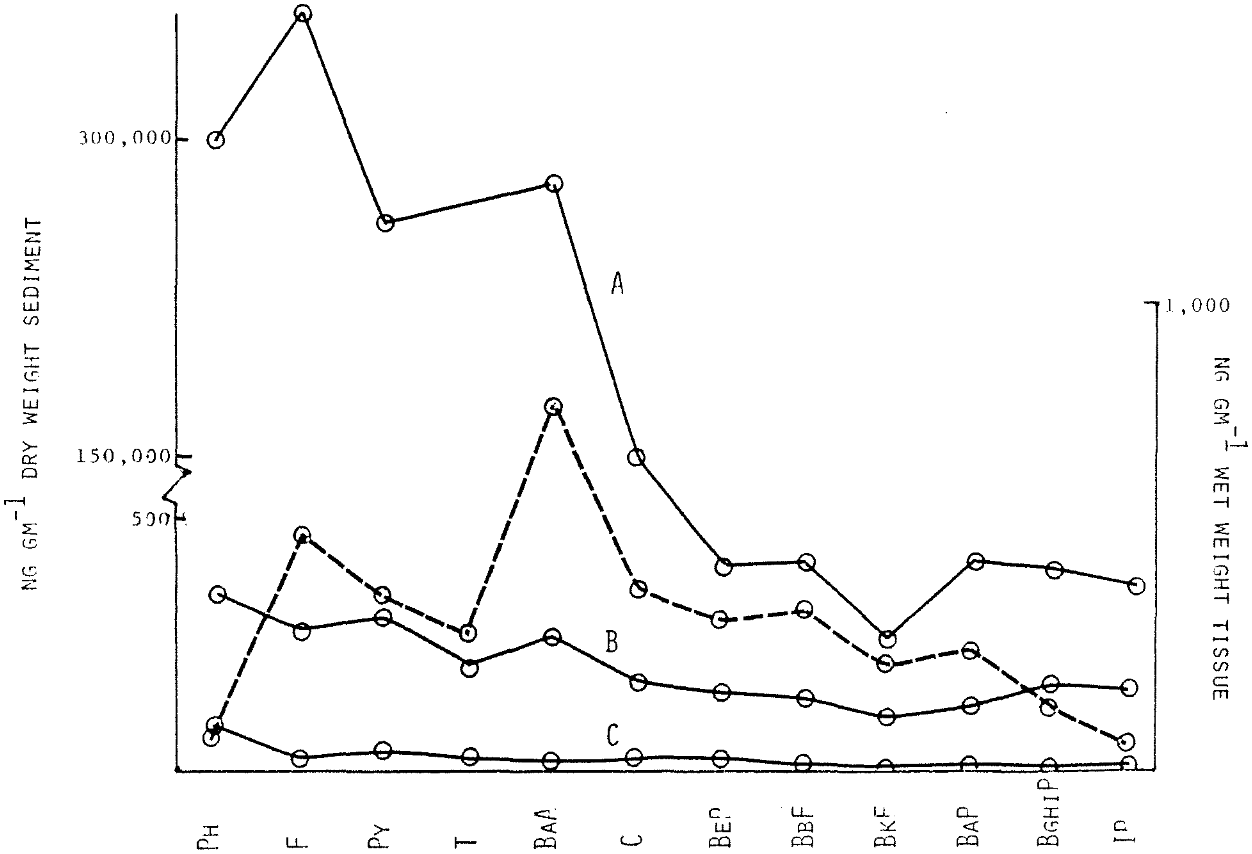


Figure 7. PAH composition profiles in contaminated bottom sediments from three Sydney Harbor locations (A - Muggah Creek, B - South Arm, C - North Arm) and bivalve mussel (dashed line). (Data from Matheson al. 1983).

Ph=phenanthrene; F=fluoranthene; Py=Pyrene; T=Triphenylene; BaA=Benzo(a)anthracene; C=Chrysene; BeP=Benzo(e)pyrene; BbF=Benzo(f)fluoranthene; BkF=benzo(k)fluoranthene; BaP=Benzo(a)pyrene; BghiP=Benzo(ghi)perylene; IP=Indeno(1,2,3-cd)pyrene.

taken by cores. They have speculated that the surface sediments may not contain the highest PAH content, and that higher concentrations may well be found below the surface, below 3 cms.

When compared to other contaminated sediments, the total PAH measured at the most contaminated station (2,830 mg $kg^{-1}$, at #29 near the mouth of Muggah Creek) is more than 20 times higher than the highest reported from Boston Harbor (Sirota et al. 1983).

Typical profiles of PAH composition in harbor sediments are shown in Figure 7. Very high values of phenanthrene, fluoranthene, pyrene, triphenylene, and benzo-a-anthracene dominated the profile in sediments near the mouth of Muggah Creek. Benzo-a-pyrene, a known mutagenic PAH, was present in all samples.

OceanChem (1986) has analyzed bottom sediments from the outer harbor for "total oil and grease", PAH and nitrogen-containing PAH (pyridine, indole, quinoline, carbazole), trace metals, and PCB and DDT. No DDT type pesticides were detected. PCB concentrations were reportedly within federal guidelines.

PAH concentrations for the outer harbor sediments were all low. Exceptions were from three sampling sites that lay nearest the mouth of Muggah Creek (their stations C861, C862, C864). OceanChem speculates on a mechanism of transport of contaminated sediments from the Muggah Creek source downstream that would involve their deposition into the outer harbor near C861 to C864. They also suggest that such sediments may then become resuspended and redeposited further down the outer harbor into a second area of high PAH concentrations.

Concentrations of the N-containing PAHs pyridine, indole and quinoline were low for all sediments analyzed. However, a relatively high concentration of carbazole was found in the C861 core, corresponding to the generally high PAH contamination at that location.

Table 6

Total major metals, trace metals and selected trace metals in Muggah Creek intertidal sediments downstream from the tarpond (ng $g^{-1}$ dry weight) (Data from Hutcheson et al., 1986)

| | Sampling station (1) | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 7 | 11 | 15 | 18 | 20 |
| major metals | 174,200 | 198,000 | 283,790 | 82,400 | 130,000 | 193,800 |
| trace metals | >1,500 | 325 | 13,760 | 1,250 | 13,690 | 1,820 |
| arsenic | 33 | 9 | 60 | 29 | 105 | 33 |
| chromium | 45 | 22 | 287 | 28 | 92 | 60 |
| copper | 341 | 51 | 1,240 | 156 | 1,855 | 220 |
| lead | 627 | 43 | 1,070 | 188 | 1,965 | 488 |
| zinc | 296 | 121 | 10,500 | 746 | 9,330 | 833 |

(1) #1 at mouth of Muggah Creek, #20 at tar pond outfall, #7-18 intermediate

7.2.2 Heavy metals

The high levels of major and trace metals in the South Arm are consistent with the industrial sources in the area (Table 6). Of particular concern are the high levels of arsenic and zinc which exceed the ocean dumping limits (Hutcheson et al., 1986). Trace metal concentrations in the outer harbor bottom sediments were either lower than or well within typical concentration ranges of metals determined for other Atlantic harbor sediments (e.g. OceanChem, 1985).

## 7.3 Tissue Contamination

7.3.1 PAH in mussel (Matheson et al., 1983)

A survey of tissue PAH loading in mussels (*Mytilus edulis*, *Volsella modiolus*) collected from ten locations around the estuary revealed PAH contamination in all samples (Table 7). Tissue PAH burdens (1) in a very general sense tended to reflect sediment concentrations, ranging between 230 and 4,100 ng $gm^{-1}$ wet weight. Lowest tissue values were reported from the outer Sydney Harbor and from the Northwest Arm, while highest concentrations were found in samples from near Muggah Creek (M6, M8).

Table 7

Correspondence between PAH body burdens in mussels (*Mytilus edulis*, *Volsella modiolus*) and PAH concentrations in nearby bottom sediments.

| Sampling site (1) | sediment (ng $gm^{-1}$ dry weight) | mussel (ng $gm^{-1}$ wet weight) *V. modiolus* | *M. edulis* |
|---|---|---|---|
| M1 (outer harbor) | 670 | 470 | |
| M12 (NW Arm) | 6,100 | 230 | |
| M10 | 13,000 | 2,700 | |
| M7 | 26,000 | 2,400 | |
| M2 | 39,000 | 1,700 | |
| M3 | 65,000 | | 740 |
| M4 | 79,000 | 3,500 | |
| M8 | 130,000 | 3,800 | |
| M6 | 200,000 | | 4,100 |
| M11 | 750,000 | 480 | |

(1) Except for sites M1 and M12, all sampling sites were from the South Arm. For location of sampling stations refer to citation. PAH concentrations are sums of 12 PAH peaks. (After Matheson et al., 1983)

The fact that mussel PAH burdens for the entire estuary are relatively consistent suggests that contamination from the Muggah Creek tar pond is not restricted to downstream portions of the harbor, but that the waters of the entire South Arm were contaminated, both downstream and upstream from the mouth of Muggah Creek. The exception was site M3, the most landward site in the South Arm, where mussel contamination was markedly lower, probably because of freshwater inflow at this point.

It is interesting from a bioavailability point of view that the compositional pattern of PAH contamination in mussel tissues does not reflect the PAH composition in the sediments (Figure 7, Table 8), in that phenanthrene is dominant in the sediments, relative to the other PAH, but is least in the tissues where it occurs in the same concentrations as indeno(1,2,3-cd)pyrene. This may just be an experimental artifact, or it may suggest some mechanism of preferential exclusion of some PAH as phenanthrene.

Table 8
Concentrations of coal-tar PAH in mussels (M. edulis) and bottom sediments from South Arm of Sydney Harbor (Matheson et al., 1983).

| PAH | M. edulis (1) | sediment (2) | tissue: sediment |
|---|---|---|---|
| phenanthrene | 70 | 14,000 | .50 |
| fluoranthene | 560 | 28,000 | 2.00 |
| pyrene | 410 | 23,000 | 1.78 |
| triphenylene | 310 | 12,000 | 2.58 |
| benzo(a)anthracene | 870 | 27,000 | 3.22 |
| chrysene | 430 | 14,000 | 3.07 |
| benzo(e)pyrene | 360 | 10,000 | 3.60 |
| benzo(b)fluoranthene | 380 | 15,000 | 2.53 |
| benzo(k)fluoranthene | 250 | 8,900 | 2.81 |
| benzo(a)pyrene | 280 | 15,000 | 1.87 |
| benzo(ghi)perylene | 140 | 17,000 | .82 |
| indeno(1,2,3-cd)pyrene | 60 | 14,000 | .43 |

(1) ng $gm^{-1}$ wet weight; (2) ng $gm^{-1}$ dry weight

7.3.2 PAH in lobster (Sirota et al., 1983)

PAH contamination in lobsters taken from the South Arm was very high in comparison with samples from other areas (Table 9). PAH content in hepatopancreas decreased with distance from the South Arm, and there was a slight correspondence between bottom sediment PAH levels and tissue PAH levels in lobsters from the area. PAH concentrations in tail muscle were markedly lower, by about an order of magnitude, than in corresponding hepatopancreatic tissue. Again, highest concentrations were found in tail meat from the South Arm, with lower values in areas more distant.

Sirota et al. (1984) have reported on some follow-up work in which more lobsters were collected and analyzed on separate occasions during 1982. The levels of PAH contamination observed in those later samples varied considerably from the earlier 1981 samples, being higher in some instances and somewhat lower in others. These workers speculate that the variability may in part be due to the migratory behavior of lobsters, and that therefore the

Table 9. PAH contamination in lobster hepatopancreas and tail muscle (ng $gm^{-1}$ wet weight) from Sydney estuary (1981 survey; from Sirota et al., 1984). "a" and "b" represent two groups of five pooled animals each. For PAH abbreviations viz. Table 8 (p.28). (T = trace amount; ND = not determined).

| HC species | South Arm | | Northwest Arm | | Harbor (1) | | Outer Estuary (2) | | Outer Estuary (3) | | Mira Bay (4) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | a | b | a | b | a | b | a | b | |
| Hepatopancreas (5) | | | | | | | | | | | |
| phen | 2900 | 3470 | 700 | 780 | T | T | 990 | 1260 | 1530 | 1280 | 25 |
| fluor | 12400 | 10700 | 3030 | 2660 | 1920 | 2150 | 1910 | 2000 | 2320 | 1940 | 68 |
| pyr | 6710 | 2940 | 780 | 730 | 730 | 850 | 910 | 1260 | 1000 | 730 | T |
| triphen | 23100 | 14900 | 4440 | 4480 | 2520 | 3850 | 5890 | 5840 | 4310 | 4600 | T |
| b(a)a | 23400 | 13400 | 1620 | 1640 | 1890 | 2150 | 3010 | 3580 | 3360 | 1700 | 18 |
| chrys | 5050 | 2820 | 360 | 430 | 585 | 620 | 1000 | 895 | 840 | 478 | 6 |
| b(e)pyr | 9330 | 5060 | 465 | 415 | 635 | 650 | 1510 | 1580 | 1080 | 590 | 14 |
| b(b)flu | 2350 | 1640 | 190 | 155 | 220 | 225 | 295 | 272 | 270 | 170 | 4.5 |
| b(k)flu | 588 | 392 | 50 | 43 | 69 | 69 | 75 | 63 | 70 | 40 | 1.1 |
| b(a)pyr | 1000 | 637 | 56 | 35 | 50 | 53 | 128 | 120 | 66 | 30 | 0.7 |
| b(ghi)p | 463 | 493 | 28 | 18 | 8 | 7 | 283 | 105 | 46 | 13 | 1.9 |
| i-pyr | 855 | 787 | 66 | 38 | 70 | 75 | 205 | 140 | 70 | 36 | 3 |
| Total | 88100 | 57300 | 11800 | 11400 | 8700 | 10700 | 16200 | 17100 | 15000 | 11600 | 142 |
| Tail Muscle | | | | | | | | | | | |
| phen | 465 | 405 | 650 | 530 | T | T | 175 | 155 | T | T | 5 |
| fluor | 545 | 435 | 170 | 145 | 110 | 125 | 145 | 103 | 85 | 100 | 9 |
| pyr | 265 | 135 | 85 | 87 | 32 | 35 | 180 | 110 | 16 | 27 | ND |
| triphen | 330 | 295 | 67 | 62 | T | T | 160 | 106 | 60 | 64 | ND |
| b(a)a | 604 | 352 | 63 | 34 | 44 | 54 | 165 | 152 | 47 | 36 | 71 |
| chrys | 79 | 51 | 9 | 6.5 | 5 | 6 | 51 | 31 | 3 | 3.5 | 14 |
| b(e)pyr | 165 | 102 | 15 | 16 | 17 | 16 | 50 | 42 | T | T | 22 |
| b(b)flu | 78 | 51 | 10 | 6 | 7 | 7 | 11 | 9 | 5 | 5 | 3 |
| b(k)flu | 25 | 14 | 2.5 | 1.6 | 2 | 2.5 | 2.4 | 2.4 | 1.6 | 1.3 | 1 |
| b(a)pyr | 40 | 23 | 2 | 3.5 | 2 | 2.2 | 3.7 | 4.6 | 1.6 | 1.3 | 1 |
| b(ghi)p | 31 | 14 | 1.6 | 2.4 | 4.5 | 2.5 | 3.4 | 5 | 1.4 | 1 | 1 |
| i-pyr | 45 | 33 | 4 | 3 | 3 | 3 | 4 | 4 | 1.5 | 1.5 | 3.7 |
| Total | 2670 | 1910 | 1080 | 897 | 226 | 253 | 950 | 729 | 222 | 241 | 109 |

(1) South bar sampling site; (2) Swivel Point sampling site; (3) Petrie Point sampling site; (4) mean of two values; (5) total PAH concentrations (ng $gm^{-1}$ wet weight)- 12,500-2,830,000 South Arm; 2,450-8,220 Northwest Arm; 250-8,070 Harbor

Table 10 Benzo(a)pyrene concentrations in lobster and mussel tissues and in bottom sediments from Sydney estuary.

| | Muggah creek | Sydney River | South Arm | Northwest Arm | Outer Harbor | "Clean site" | |
|---|---|---|---|---|---|---|---|
| SEDIMENTS (1) | 0.59-68 | - | - | - | - | - | (3) |
| | 99-110 | 0.89-15 | 0.75-22 | 0.076-0.35 | 0.005-0.27 | | |
| | - | - | - | - | 0.014-1.7 | - | (4) |
| | - | 2.0-3.8 | 0.77-180 | 0.06-1.5 | 0.56-1.2 | - | (5) |
| MUSSEL (2) | - | 18-280 | 10-140 | 6.3 | 25 | - | (4) |
| (2) | - | - | - | - | 195-226 | 0.2-5 | (6) |
| LOBSTER (2) (d) | | | | | | | |
| hepatopancreas | - | - | 387-2240 | 35-147 | 53-160 | 0.4-24 | |
| tail | - | - | 8-55 | 2-6.7 | 1.7-4.7 | 0.5-2.7 | |
| pincer | - | - | 8.5-45 | - | - | - | |
| claw | - | - | 11-58 | - | - | - | |

(1) ug $g^{-1}$ dry weight; (2) ng $g^{-1}$ wet weight; (3) Hutcheson et al., unpub. report; (4) Matheson et al., 1983; (5) Packman et al., unpub. report; (6) Sirota et al., 1984

correspondence between lobster PAH and sediment PAH is at best somewhat tenuous. Another possible source of error or uncertainty may lie with the UV/fluorescence detection technique which these workers correctly point out may be influenced by the presence of other fluorescing materials. While the variability was a factor, nonetheless these values reflected generally the differences in contamination seen in the different sampling sites.

MacCubbin et al. (1986) have further characterized some of the PAH contamination in polar and nonpolar extracts of lobster tissues from Sydney harbor. This work was in support of some toxicity bioassay studies involving the use of trout embryos. Their estimates of PAH concentrations in lobster tissues are essentially similar to the findings reported earlier by Sirota et al. (1983, 1984).

It is again interesting to note, as was noted for bivalve PAH contamination above, that the tissue PAH profile does not parallel the sediment PAH profile. Again, phenanthrene is present in tissues in correspondingly lesser concentrations relative to other tissue PAH levels than is the case in corresponding contaminated bottom sediments.

Concentrations of the mutagenic PAH benzo(a)pyrene (BaP) in tissues generally reflect PAH and BaP loadings in bottom sediments, and vary directly with distance from Muggah Creek where highest BaP concentrations are found (Table 10). For example, concentrations of BaP in hepatopancreas of South Arm lobsters were 636 and 1000 ng $gm^{-1}$ wet weight in duplicate samples. By comparison, BaP levels in lobster from so-called "clean" or "control" areas (Port Morien, Guysborough, Louisburg) were between 1.6 and 30 ng $gm^{-1}$ wet weight in hepatopancreas, and between 0.5 and 2.7 ng $gm^{-1}$ wet weight in tail muscle.

Detectable levels of BaP were obtained even in mussels and lobsters from the outer harbor, indicating uniform contamination through the system.

### 7.3.3 Metals in tissues

No data have been reported on metal concentrations in biota from the harbor or larger estuary.

## 8. CONTAMINANT EFFECTS IN SYDNEY ESTUARY

### 8.1 Mutagenic Potential and Toxicity of Tarpond Derived PAH

Interest in the mutagenic/carcinogenic potential of the tarpond PAH arises from the presence of high to very high concentrations of several known mutagenic PAH in the tar pond material.

### 8.1.1 Mutagenicity in waste flow from Sysco mill

Waste flows from the Sysco mill were reportedly highly mutagenic or otherwise genotoxic (Hildebrand, 1982). The latter cites unreferenced tests showing that Sysco waste flows were mutagenic in the so-called Ames *Salmonella*/microsome test, exhibited chromosome-damaging activity in ovary cells of Chinese hamsters, elicited unscheduled DNA synthesis and also inhibited DNA repair in diploid human fibroblast cells in laboratory cultures.

### 8.1.2 Mutagenicity in coke plant effluent

Effluent from the coke plant was similarly found to be mutagenic (Payne, unpub. data, cited in Hildebrand, 1982), although no experimental or assay details are available.

### 8.1.3 Mutagenicity in tar pond effluent

Extracts of effluent from the tar pond itself were reportedly mutagenic in several tests, including the Ames *Salmonella*/microsome test using the Ames bacterial strain TA100, with S9 activation (C.f.) (cited in Odense, 1982).

8.1.4 Mutagenicity in mussel extracts

Odense (1982) has investigated, in some detail, the likely mutagenic potential in extracts of mussels collected from several polluted harbors in Nova Scotia. The rationale for this work was the notion that mussels being very efficient filter feeders, these organisms would serve to concentrate in their tissues any mutagenic PAH present in the water column. Using the Ames Salmonella/microsome test, Odense tested aqueous, ethanolic and chloroform-methanol extracts of mussels, but was unable to detect significant mutagenicity, in either activated or unactivated tissue extracts. He suggested that his inability to detect tissue mutagens may not be due to any absence of mutagens, but that the Ames test may not be sensitive enough to detect mutagens in field collected tissues.

8.1.5 Mutagenicity/toxicity in Muggah Creek sediments

In a later parallel investigation, Hutcheson et al. (1986) and Odense et al. (unpublished manuscript) have reported on the positive mutagenic activity in sediments from Muggah Creek, downstream of the tar pond. Sediment samples were collected from the low intertidal zone at twenty sites and were solvent-extracted to provide three fractions - a neutral, acid, and alkaline extract. These were tested using the bacterial strains (S. typhimurium) TA100 and TA102 (for base pair mutations) and TA97a and TA98 (for frameshift mutations).

All tests with TA97a and TA98 strains proved highly mutagenic when compared to controls, with greatest mutagenic response in activated alkaline

C.f. Some compounds are not mutagenic until chemically altered or "activated" by certain enzymes, as found in the S9 microsomal fraction of mammalian liver. In practice, the test is run without and without an S9 preparation prepared from rat liver.

sediment extracts (Figure 8). No mutagenic activity was obtained with the base-pair sensitive strains. Interestingly, sediments from the junction of Muggah creek and the South Arm, i.e. the most distant tested, proved highly toxic to the test strains in their assays. Highest mutagenic responses were obtained with sediments taken from mid-way Muggah Creek. Sediments from site 20, directly near the outfall of the tarpond were slightly less mutagenic than the midway samples.

To further evaluate the toxic aspect of these results, cultures of the ciliate Blepherisma sp. were grown with seawater extracts of Muggah Creek sediments, and monitored for six days. The results (Table 11) tended to follow the mutagenic responses obtained above (viz. Table 10). Sediments from several sites proved toxic to highly toxic to Blepherisma. Highest toxicity was obtained at the midway sites #7, 11, and 15. No toxicity was observed at site #1, at the junction with the South Arm. The site directly near the tar pond outfall also proved highly toxic to growth after four days.

Table 11

Toxicity of seawater extracts of Muggah Creek intertidal sediments to growth of the ciliate Blepherisma sp. Results given are ratios of growth in sediment extracts to growth in seawater controls.

| Sample site | day 1 | 3 | 4 | 6 |
|---|---|---|---|---|
| #1 | 121% | | 128% | 119% |
| #7 | 35 | | 4 | 12 |
| #11 | 109 | 37 | | 9 |
| #15 | 70 | 17 | | 5 |
| #18 | 86 | | 98 | 70 |
| # | 110 | | 143 | 180 |
| #20 | 168 | | 38 | 22 |

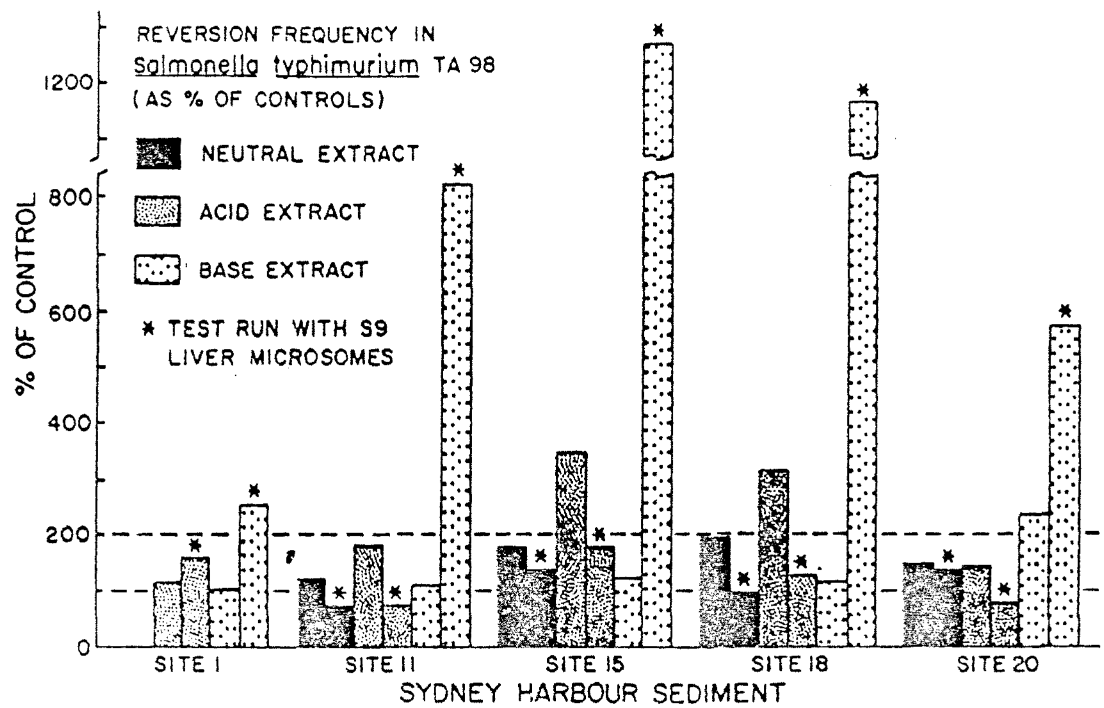


Figure 8. Mutagenicity in solvent fractions of sediment from Muggah Creek. Results from Ames' Salmonella/microsome assay using strain TA98. Dotted line at 100 indicates spontaneous reversion in controls. Dotted line at 200 indicates doubling of revertants.

However, results from similar toxicity assays with the green alga Dunaliella tertiolecta were less clear. Short-term (4-day) algal growth in culture media containing sediment extracts was reduced by up to 58% of controls, but responses were inconsistent. Long-term (30-day) incubations in sediment extract did not show inhibition or changes in viability.

Odense and co-workers reviewed these results in terms of their contaminant analysis of intertidal sediments, taken from the same locations (viz. Tables 5, 6). All sites contained a range of PAH and other organic contaminants, distributed in a marked gradient, with highest values near the tar pond outfall and lowest values near the mouth of Muggah Creek. Unlike the clear correspondence between toxicity and mutagenicity, there was no such clear correlation between contaminant concentration and either toxicity or S-9 activated mutagenic potential. Odense et al suggest this to be due, in part, to masking of mutagenicity by the presence of toxic components.

Water from Muggah Creek has been reported (Hildebrand, 1982) to be acutely toxic to test fish Fundulus heteroclitus, with an $LT_{50}$ of 13 hours to 100% mortality. No other data is available on the water quality from the harbor.

The toxicity of the hydrocarbon material available to biota from the harbor was investigated by MacCubbin et al. (1986) using extracts of lobster hepatopancreas taken from the area. One microliter aliquots of polar and non-polar extracts of hepatopancreas were then injected into the yolksac of rainbow trout embryos at the one-eyed stage. Survival over 90 days post-injection was then compared with control which received only solvent or received extract from "clean" lobsters.

Of the two fractions, the polar fraction, containing an unidentified suite of compounds, was most toxic and caused mortality over the exposure period (Table 12). Mortality was significantly higher than in either solvent

Table 12

Toxicity of Sydney Harbor lobster hepatopancreas (h.p.) extract to rainbow trout embryos. One-eyed stage embryos were injected into the yolk-sac with 1 uL aliquots of polar or non-polar solvent extracts of hepatopancreas. Controls received solvent only or extract of "clean" hepatopancreas.

| Treatment | Polar fraction mortality (%) | | Non-polar fraction mortality (%) | |
|---|---|---|---|---|
| | egg stage | fry stage | egg stage | fry stage |
| Controls: | | | | |
| solvent only | 0.0 % | 12.5 % | 0.0 % | 13.0 % |
| "clean" control | 0.0 | 13.5 | 0.0 | 15.5 |
| Contaminated h.p.: | | | | |
| 1% extract | 8.0 | 21.7 | 17.0 | 27.7 |
| 10% " | 9.0 | 31.9 | 2.0 | 23.5 |
| 100% " | 66.5 | 34.3 | 4.9 | 12.8 |

blank controls or in embryos that had received polar extract of "clean" hepatopancreas. Mortality increased directly with dosage. The non-polar fraction, containing the bulk of the PAH, was slightly less toxic.

These workers surmised that the surprisingly higher toxicity of the polar fraction, i.e. not containing PAH, might be due to some unidentified PAH metabolites. Lobsters are known to be capable of PAH metabolism, and the hepatopancreas is the central concentration site for toxicants and their metabolic derivative.

## 8.2 Histopathological Effects

No rigorous observations have been carried out on the occurrence of superficial or tissue abnormalities - skin tumors or lesions, liver lesions, neoplasia. However, MacCubbin et al. (1986) report very briefly that bile duct hyperplasia was present in high-dosage fish from the above lobster hepatopancreas-trout embryo assay at 8 months post-injection. This was observed apparently in fish injected with either polar or non-polar fractions.

## 8.3 Ecosystem Level Effects

Very few data exist on the quality of benthic organisms or communities. A 1979 benthic fauna survey by the College of Cape Breton (primarily South Arm) and a 1981 survey by EPS (Northwest Arm, South Arm, inner harbor) have provided the only information available, and give some insight into the benthic water quality.

The Northwest Arm showed a higher diversity of taxa than in the South Arm, and contained a number of species not present in the latter - hermit crabs, limpets and amphipods. The South Arm benthic community was dominated by predatory polychaetes and sea anemones. In Muggah Creek itself, the tidal flats of the creek were devoid of living organisms. Generally, both diversity and abundance of benthic organisms increased with distance from Muggah Creek.

## 8.4 Impact on Fisheries

While the fishery has recently been closed because of the high PAH values reported from lobsters, there appears to have been no noticeable environmental/toxic impact on the fishery. Lobstering is the principal fishery in the estuary. There is no commercial finfishery, but herring, mackerel and cod and flounder occur within the greater estuary.

No reports have come in of tainting or other indications of PAH-induced defects in fish quality from these waters.

# 9. DISCUSSION

The studies and data reviewed above very clearly indicate considerable to very high contamination by PAH in the entire estuary, as well as high to very high levels of metals and other contaminants (PCB, organic synthetics) in at least Muggah Creek. It is highly likely that the latter also occur in other parts of the estuary. Generally, biota in the estuary (bottom fish, lobster, mussels) seem to reflect the PAH distributions, with highest contamination found in or near the Muggah Creek PAH source.

However, the literature todate with respect to PAH pollution of the estuary is unfortunately lacking in a number of aspects - a) there is insufficient correspondence between data from different studies, b) an obvious lack of a consistent set of PAH data by depth for sediment cores, and c) the absence of a synoptic set of PAH data for the water column, including surface levels. This has meant that the available data, while providing a reasonable first estimate of PAH contamination of the system, is insufficient to model PAH transport within the system. It is also insufficient to confidently predict the long-term persistence of these compounds in bottom sediments, and therefore the long-term susceptibility of biota to PAH contamination.

From what is known of the estuary and its pollution history, and of the physical/chemical properties of these various contaminants one can expect that the bottom sediments of both the South Arm, Northwest Arm and the nearby or inner harbor are contaminated, possibly to a considerable depth (>10 cm). Given the dye patch behavior and the reports of high PAH concentrations in the inner and outer harbor, it is likely that some areas will contain very high contaminant levels, acting as "hot spots".

It is also likely that, even with cleanup of the tar pond, that the contamination of the bottom sediments will persist for a considerable length of time, possibly for several decades or longer. Any evaluation of such self-cleaning potential, as by tidal flushing, will require more information on bottom currents, and sediment grain size and movements, as well as more information on bottom sediment contaminants.

At present, it seems likely that all biota in the estuary are contaminated by tarpond effluent. After the proposed cleanup, the risk of continuing contamination to bottom-dwelling and pelagic biota in the estuary depends to some extent on the remobilization of contaminants from the bottom sediments. At this moment there is insufficient information on such remobilization, but it is anticipated that at least the bottom-dwelling biota - flounder, lobster - will continue to become contaminated through extensive contact with the contaminated bottom sediments.

One very worrisome set of observations, from an environmental threshold point of view, is the small data set on the mutagenic potential reported for extracts of lobster hepatopancreas and for Muggah Creek intertidal sediments. Yet these results show a) the presence of mutagenic materials in considerable quantities in sediments and biota, and point to the possibility of b) extensive mutagenic dispersal throughout the estuary, and c) that any assimilative capacity for the system has been exceeded, i.e. the estuary is overloaded with regards to mutagenic components. One complicating factor is that the mix of contaminants enhances the mutagenic/tumorigenic risk, while at the same time confusing the response in bioassays because of the interacting presence of both toxic and mutagenic components. Despite the possibility of this extra hazard, one particularly critical biological end-point, the bottom fishery, has not been evaluated for environmental tumorigenesis.

Given the evidence available, the data base for contamination of this estuary is remarkably small with some very obvious gaps. Principal among these are 1) the absence of data on contamination of the water column (already referred to above) and 2) the lack of oceanographic information. The former is the primary transport route for contaminant flow through the system, and any attempts at determining pollutant loading or its eventual fate within the estuary requires a knowledge of flow and transport rates in the water column. The lack of an oceanographic data base is at least as serious, and is probably the first information that needs to be accumulated in order to provide an understanding of contaminant turnover in and export from the system. Without a firm hydraulic circulation model for the estuary, all other pollutant data will remain a serious of unconnected data points. Already remarked on above is 3) the absence of information on the depth to which the bottom sediments have become contaminated. Interesting in this respect is the observation by Matheson et al. (1983) that PAH concentrations in grab samples (which sample the top 5 to 10 cms) were consistently higher than in the surface 2 cm of core samples. The depth of contamination together with detailed concentrations would allow the calculation of contaminant loading in the estuary sediments. Together with contaminant degradation times and data on sediment-water column interaction (obtained from the oceanographic survey) this would allow some estimates of long-term persistence. 4) Aside from the single data set obtained by the College of Cape Breton, there are no comprehensive data on benthic communities which might correlate with bottom sediment contamination. Yet, data on benthic community composition are probably the most informative and most easily gathered index of environmental and degradation/recovery. Finally, 5) there is the very obvious lack of a comprehensive set of data for heavy metal contamination in tissues and the water column. This in part has been because of the strong emphasis on the tar PAH, while simultaneous toxicity/mutagenicity by heavy metals has been ignored. However, their high levels in concordance with high PAH levels raise the likelihood of synergistic toxicity and/or mutagenicity as has been described for Puget Sound.

In final analysis, given the data reviewed here, it appears that the system is working rather predictably in terms of where the contaminants reside and their bioavailability. It is anticipated that the water column in the harbor will likely contain low PAH concentrations, except for in and near Muggah Creek, and that the primary route of contaminant dispersal is via suspended particulate matter. Thus the bottom sediments likely act as contaminant sinks, as is evidenced by high contaminant levels, up to three to four orders of magnitude greater than in tissues. Information on effects is minimal, but available observations on tissue contaminant levels and the mutagenic capacity in some compartments suggest that parts of the system at least are now overloaded. Recovery time by natural processes to the condition of uncontaminated sediments, even with removal of the tar pond, is likely to be in the order of decades to centuries.

Any physical activity in the tar ponds, such as associated with proposed mechanical cleanup, will almost undoubtedly inject a high contaminant concentration pulse into the system which will be reflected in tissue and sediment contaminant loading. Any attempts at long term monitoring of the situation will need this information for predictive and monitoring purposes.

## 10. ACKNOWLEDGMENTS

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## 11. NON-SYDNEY HARBOR REFERENCES CITED

(See also Appendix A, p. 45, Chronological Listing of Reports and Studies Dealing with Contamination in Sydney Harbor and surroundings)

AMES, B. N., J. MCCANN AND E. YAMASUK. 1975. Methods for detecting carcinogens and mutagens with the _Salmonella_/mammalian microsome mutagenicity test. Mutat. Res. 31:347-364.

GUERIN, M.R., J.L. EPLER, W.H. GRIEST, B.R. CLARK AND T.K. RAO. 1978. Polycyclic aromatic hydrocarbons from fossil fuel conversion processes. _In_ Carcinogenesis, Vol. 3: Polynuclear aromatic hydrocarbons. (Jones, P.W. and P.I. Freudenthal, ed's). Raven Press, New York. pp. 21-33.

LAO, R.C., R.S. THOMAS AND J.L. MONKMAN. 1975. Computerized gas chromatographic/mass spectrometric analysis of polycyclic aromatic hydrocarbons in environmental samples. J. Chrom. 112:681-700.

MCCANN, J., E. CHAI, E. YAMASUK AND B.N. AMES. 1975. Detection of carcinogens as mutagens in the _Salmonella_/microsome test: assay of 300 chemicals. Proc. Nat. Acad. Sci., USA. 72:5135-5139.

NATIONAL ACADEMY OF SCIENCES, USA. 1972. Particulate polycyclic organic matter. Washington, D.C. pp. 13-35.

12. APPENDICES

12.1 Appendix A

Chronological Listing of Reports and Publications Dealing with Contamination in Sydney Harbor and Surroundings.

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1972 MACHELL, J.R. 1972. Walter quality survey of Sydney Harbour, N.S., 1971. Canada, EPS, Atlantic Region, Manuscript Report 72-9

1979 WENDLAND, T. 1979. 1978-79 Sydney Harbour survey; benthic fauna distribution and related studies. Environmental Technology Project, College of Cape Breton, Sydney, N.S. Unpublished project report.

1982 GUILCHER, M.P., P.H. HENNEBURY, P.A. HENNIGAR, M. MORIN, H.S. SAMANT AND G.L. TRIDER. 1982. Sources of polycyclic aromatic hydrocarbons, Sydney, Nova Scotia. Unpublished document, Environmental Protection Service, Environment Canada Atlantic Region, August 1982. 20 pp

HILDEBRAND, L.P. Environmental quality in Sydney and northeast industrial Cape Breton, Nova Scotia. Environment Canada, Atlantic Region, Environmental Protection Service Surveillance Rept. EPS-5-AR-82-3. 89 pp.

ODENSE, R.B. 1982. Measurement of the mutagenic potential in extracts of Mytilus edulis collected from polluted harbors. M.Sc. thesis. Dalhousie University, Halifax, N.S., Canada. 108 pp.

1983 MATHESON, R.A.F., G.L. Trider, W.R. Ernst, K.G. Hamilton and P.A. Hennigar. 1983. Investigation of polynuclear aromatic hydrocarbon contamination of Sydney Harbour, Nova Scotia. Surveillance Rept EPS-5-AR-83-6. Environment Canada. 86 pp.

SIROTA, G.R., J.F. Uthe, A. Sreedharan, R. Matheson, G.J. Musial and K. Hamilton. 1983. Polynuclear aromatic hydrocarbons in lobster (Homarus americanus) and sediments in the vicinity of a coking facility. In: Polynuclear aromatic hydrocarbons: Chemical analysis and biological effects. 5th International Symposium (Eds. M. Cooke and A.J. Dennis). Battelle Press, Columbus, Ohio. Pp. 1123-1136.

1984 ATWELL, L., P. Hennigar, J. Kozak, M. Morin and C. Oldreive. 1984. Ambient air polynuclear aromatic hydrocarbons study, Sydney, Nova Scotia. Surveillance Rept EPS-5-AR-84-7. Environment Canada. 79 pp.

OCEANCHEM, 1984. Examination of dredged material disposal alternatives, Sydney, N.S. Final Report. OceanChem Ltd., Dartmouth, N.S.

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|---|---|
| | SIROTA, G.R., J.F. Uthe, D.G. Robinson and C.J. Musial. 1984. Polycyclic aromatic hydrocarbons in American Lobster (Homarus americanus) and Blue Mussels (Mytilus edulis) collected in the area of Sydney Harbour, Nova Scotia. Canadian Manuscript Report of Fisheries and Aquatic Sciences, No. 1758. 22 pp. |
| 1985 | ACRES International Ltd. 1985. Sydney Tar Pond Study. Final Project Report. Volumes I, II, III. |
| | SAMANT, H.S., P.A. HENNIGAR & J.B. FAUGHT. 1985. Sydney tar pond engineering design study, quality assurance/quality control program. Environment Canada, Environmental Protection Servioce, Atlantic Region, Surveillance Report EPS-5-AR-85-4, 46 pp. |
| 1986 | HUTCHESON, M.S., D.J. Popham, R. Odense, D. Boyle, and P.J. Wangersky. 1986. Evaluation of microorganisms for assessing the toxicity of and mutagenicity of contaminated sediments. Seakem Oceanography, Final Report to Supply and Services Canada. Contract No. 03SB.KE603-3-0806. 128 pp + 2 appendices. |
| | MACCUBBIN, A.E., G.R. Sirota, L. Trzeciak and J.J. Black. 1986. Trout embryo bioassays and HPLC chromatography of polar and non-polar fractions isolated from lobster hepatopancreas. In: Polynuclear aromatic hydrocarbons: Chemistry, Characterization and Carcinogenesis. 9th International Symposium (Eds. M. Cooke and A.J. Dennis). Battelle Press, Columbus, Ohio. Pp. pp. 517-530. |
| | MACKNIGHT, S. and G. Sirota. 1986. Use of polynuclear aromatic hydrocarbon concentrations to re-define the ocean dumping permit "oil and grease" test. In: Proceed. 11th World Dredging Conference, Brighton, U.K. March 1986. pp. 587-594. |
| | OCEANCHEM Group. 1986. Sea Bottom Analysis; Outer Channel, Sydney, N.S. Prepared for Public Works Canada, Atlantic Region. Project 701510. |
| Other | ODENSE, R.B., M.S. Hutcheson, J.D. Popham and B.F. Fowler. Mutagenicity and toxicity of PAH contaminated marine sediment. Unpublished manuscript. |
| In Press | UTHE, J.F. and C.J. Musial. Polycyclic aromatic hydrocarbon contamination of American Lobster (Homarus americanus) in the proximity of a coal-coking plant. Bull. Environ. Contam. Toxicol. (In Press). |
| In Prep'n | PACKMAN, G.A., K.L. TAY, P. HENNIGAR AND B. HORNE. Examination of potential dredge spoils and disposal sites in Sydney Harbour, Nova Scotia. Environmental Protection Service, Environment Canada, Atlantic Region. Draft document, 45 pp. |

12.2 Appendix B

Chronological Listing of Projects in Sydney Harbour Area.

| | | |
|---|---|---|
| 1971 | Water pollution survey, Sydney Hbr | Machell (1972) |
| 1977 | Coal mining effluent, monitoring program for N.B. and N.S. | EPS (Day et al., 1979) |
| 1979 | Benthic biota & metals survey, South Arm, Northwest Arm | Col. of Cape Breton (Wendland, 1979) |
| 1979, 1980 | Sysco raw waste, pollutant parameters | EPS (Hildebrand, 1982) |
| 1980, 1981 | PAH measurements, lobster | DFO (Sirota et al., 1983a, b) |
| 1981 | Benthic biota and pollutant survey, South Arm, Northwest Arm | EPS (Hildebrand, 1982) |
| | Environmental evaluation study - dye flow study, regional waste contaminant survey, tar pond analysis, sediment, lobster, mussel PAH survey, PAH analyses, pollutant screening in benthic cores | EPS (Matheson, 1983) |
| 1982 | PAH sources, Sydney Hbr | EPS (Guilcher et al. 1982) |
| | Listing of accidental hazardous spills harbor area | EPS (Hildebrand, 1982) |
| | Mutagenicity and toxicity studies, Muggah Creek sediment extracts | Odense et al. (unpub. ms.); Hutcheson et al. (1986) |
| 1983 | Tar pond study | Acres (1985) |
| 1984 | Dredge materials, chemistry | OceanChem (1984) |
| 198- | Genotoxicity of Sydney Harbor lobster hepatopancreas extracts | MacCubbin et al. (1986) |
| 1985 | Quality assurance/quality control Tar pond engineering design study | Samant et al. (1985) |
| 1986 | Sea bottom chemical analysis, outer harbor | OceanChem (1986) |
| 1987 | Dredge material, chemistry | EPS (Packman et al.) |

12.3 Appendix C

Archival Location of Data Sets for Sydney Harbor.

| Data | Geographic location | Literature source | Page |
|---|---|---|---|
| BENTHIC FAUNA | | | |
| survey | South & NW Arms, 1979 | Hildebrand (1982) | 66-72 |
| LOBSTER | | | |
| PAH | estuary | Sirota et al. (1984) | 108-119 |
| MUSSELS | | | |
| PAH | estuary | Matheson et al. (1983) | 81-91 |
| | | Sirota et al. (1984) | 108-119 |
| METALS | | | |
| sediments | Sydney Harbor, 1979 | Hildebrand (1982) | 66-72 |
| | | Packman et al. (1) | 99-107 |
| " | South/NW Arms | Wendland (1979) (2) | 120-123 |
| sediments | downstream Muggah Creek | Hutcheson et al (1986) | 73-80 |
| cores | outer estuary | OceanChem (1986) | 92-97 |
| grabs | estuary | " " | |
| OIL & GREASE | | | |
| cores | outer estuary | OceanChem (1986) | 92-97 |
| | | OceanChem (1984) | 120-123 |
| PAH | | | |
| sediments | downstream Muggah Creek | Hutcheson et al. (1986) | 73-80 |
| | | Odense et al. (1) | 98 |
| sediments | estuary | Matheson et al. (1983) | 81-91 |
| | | Packman et al. (1) | 99-107 |
| cores | outer estuary | OceanChem (1986) | 92-97 |
| grab samples | estuary | " " | |
| lobster | estuary | Sirota et al. (1984) | 108-119 |
| mussels | estuary | Matheson et al. (1983) | 81-91 |
| | | Sirota et al. (1984) | 108-119 |
| N-PAH | | | |
| cores | estuary | OceanChem (1986) | 92-97 |
| PCB's etc. | | | |
| sediments | downstream Muggah Creek | Hutcheson et al. (1986) | 73-80 |
| | estuary | OceanChem (1986) | 92-97 |
| | | OceanChem (1984) | 120-123 |
| SEDIMENT GRAIN SIZE | | | |
| sediments | estuary | Packman et al. (1) | 99-107 |
| | | OceanChem (1986) | 92-97 |
| | | OceanChem (1984) | 120-123 |

(1) unpublished manuscript; (2) cited in OceanChem (1984)