DETERMINATION OF CARBON BLACK IN URBAN AIR

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ABSTRACT

The City of Hamilton is one of the most heavily industrialized cities in Canada. In recent years, residents of communities in the east-end of Hamilton have complained about "black fallout" on their properties; this air particulate deposition takes the form of a fine, greasy black film that coats their houses, cars, etc. A carbon black production company has been suspected as the primary source of this black particulate, although there are other potential sources of black particulate, including emissions from two large steel industries, vehicular traffic and other sources.

One of the major problems that has faced the Ministry of the Environment (MOE) in dealing with public complaints regarding "black fallout" has been the lack of an analytical procedure that would allow carbon black and other types of "black fallout" to be distinguished. My focus has been to develop the first analytical methodology to identify and quantify carbon black in ambient air. This approach to the determination of ambient levels of carbon black is based upon a sequential extraction methodology and the gas chromatography-mass spectrometric (GC-MS) quantification of an unusual polycyclic aromatic compound (PAC) I have identified on carbon blacks (thiacoronene) as a source tracer for carbon black.

In an air monitoring study carried out from 1995 to 1998, I have been able to identify and quantify carbon black in ambient air samples collected downwind of a carbon black production plant, which varied from 0.01 to 1.43 μg carbon black/m^3 of air.

All concentrations of carbon black were well above the method detection limit of 0.004 $\mu g/m^3$ with an uncertainty estimate of less than 5%. In the evaluation of sources of "black fallout" other than carbon black, I investigated a new source apportionment strategy based on a manganese-tin (Mn-Sn) metal index to differentiate levels of steel industry impacts in ambient air.

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LIST OF ABBREVIATIONS

amu	atomic mass unit
B21T	benzo[b]naphtho[2,1-d]thiophene
B23T	benzo[b]naphtho[2,3-d]thiophene
cm	centimeter
Da	Daltons
DCM	dichloromethane
DW	downwind
EC	Environment Canada
EI	electron impact
EIC	extracted ion chromatogram
EPA	Environmental Protection Agency
ft^3	cubic feet
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
HAQI	Hamilton-Wentworth Air Quality Initiative
hr	hour
HRMS	high resolution mass spectrometry
HPLC	high performance liquid chromatography
HWY	highway
i.d.	internal diameter
km	kilometer

L	liter
LC	liquid chromatography
log	logarithmic
M	molecular mass
m	meter
m/z	mass-to-charge ratio
m^3	cubic meter
mg	milligram
µg	microgram
mL	milliliter
µL	microliter
mm	millimeter
µm	micrometer
MOE	Ontario Ministry of the Environment
ng	nanogram
NIST	National Institute of Standards and Technology
nm	nanometer
NPRI	National Pollutants Release Inventory
PAC	polycyclic aromatic compound(s)
PAH	polycyclic aromatic hydrocarbon(s)
PASH	polycyclic aromatic sulfur heterocycle(s)

pg	picogram
PM_{10}	respirable particulate matter, < 10 μm in diameter
R^2	coefficient of determination
R234	234 Da thia-arene ratio
R258	258 Da thia-arene ratio
RBG	Royal Botanical Gardens
RSD	relative standard deviation
SH	sulfur-hydrogen
SIM	selected ion monitoring
SRM	Standard Reference Material
TCor	thiacoronene
TIC	total ion chromatogram
TOL	toluene
TPAC	total concentration of polycyclic aromatic compounds
TSP	total suspended particulate
US, U.S.A.	United States of America
UV	ultraviolet
UW	upwind
Vis	visible
v/v	volume to volume ratio

1. INTRODUCTION

The City of Hamilton is the seventh largest Canadian urban centre (approximate population: 460,000) and one of the most heavily industrialized cities in the country. In recent years, residents of communities in the east-end of Hamilton have complained about "black fallout" on their properties; this air particulate deposition takes the form of a fine, greasy black film that coats their houses, cars, etc. A carbon black production company located in the east-end of Hamilton has been suspected as the primary source of this black particulate, although there are other potential sources of black particulate including emissions from two large steel industries, vehicular traffic and from other sources.

One of the major problems that has faced the Ministry of the Environment (MOE) in dealing with public complaints regarding "black fallout" has been the lack of an analytical procedure that would allow carbon black and other types of "black fallout" to be distinguished. Our focus has been to develop the first analytical methodology to identify and quantify carbon black in ambient air.

1.1. URBAN AIR POLLUTION

1.1.1. Sources of Air Particulate

"Black fallout" is composed of black particulate matter that is deposited from the air onto the ground and water. Some particulate matter is created in the atmosphere by chemical reactions among gases and vapors and some is created from anthropogenic activities. Fine particles created in the atmosphere are primarily composed of sulfates,

nitrates, organics, ammonium, and lead compounds. Coarser particles can be introduced to the atmosphere as solids from the surface of the earth and the seas; these are primarily composed of silicon, iron, aluminum, sea salt and plant particles. The particles can coagulate, grow larger and eventually are scavenged by the atmosphere through sedimentation or rainout when there is precipitation.[1-3]

The majority of particles in the atmosphere are roughly spherical in shape because they are formed by condensation or cooling processes or because they contain core nuclei coated with liquid. Liquid surface tension draws the material in the particle into a spherical shape. Liquids coating the particles can contain the aldehydes, ketones, acids, polycyclic aromatic compounds (PAC) and trace metals as well as unburned fuels from inefficient combustion processes. The liquid nature of some particle surfaces affects the relative adsorption of compounds to the particulate.

Urban air contains a wide range of airborne particulate which come from many sources of pollution such as combustion emissions, wind-blown dust from roads, construction sites and agricultural areas, ash from forest fires and emissions from industries. Some particulates are emitted directly into the air by diesel and gasoline engines, fuel combustion, power plants, and a range of industrial processes.[3-5] The composition of particles from combustion processes includes soot or carbonaceous material, trace metals, sulfates, aldehydes and ketones, acids and polycyclic aromatic compounds.[1,6] Industrial sources are stationary and tend to emit relatively consistent qualities and quantities of pollutants as opposed to the variable emissions from mobile sources which include automobiles, trucks and buses, aircraft, watercraft, trains and tractors. [1,6]

1.1.2. Inhalable Air Particulate and Health Effects

Mechanically generated particles from agriculture, mining, road traffic, and related sources are generally larger than 2.5 μm in aerodynamic diameter. These are usually referred to as coarse mass particles. In contrast, particles resulting from combustion processes are generally less than 2.5 μm in aerodynamic diameter (called respirable particulate or $PM_{2.5}$). Recent epidemiologic studies in 17 cities on three continents have consistently reported increased daily mortality associated with exposures to particulate air pollution.[3] The strongest association was found with $PM_{2.5}$, that is combustion-related particles.

In response to increasing concerns over the health risks related to exposures to respirable airborne particulate, the U.S. Environmental Protection Agency (EPA) established a program for the monitoring of inhalable particulate (particulate matter of 10 microns or less, called PM-10).[7,8] This monitoring now includes $PM_{2.5}$. In Canada, the Hazardous Contaminants Technical Committee of the Ontario Ministry of the Environment assigned high priority to the study of polycyclic aromatic hydrocarbons. Since 1971, the Ministry has been conducting province-wide surveys of PAH levels in the ambient air of major urban and industrial centres in Ontario, including the City of Hamilton.[9] Monitoring by the ministry has also included Total Suspended Particulates (TSP) in the air as well as oxides of sulfur (SOx) and nitrogen (NOx) and other gases.

Approximately 40 - 60% of TSP is composed of inhalable particulate. The MOE has proposed an interim 24-hour average ambient air quality criterion of 50 $\mu g/m^3$ for inhalable particulates. On average, industries in the urban areas of Hamilton can add

approximately 30-40 $\mu g/m^3$ of inhalable particulates to the air concentrations downwind.[10] In typical urban areas, long-range transport can contribute approximately 55% to the inhalable particulate levels on an annual basis, urban sources account for approximately 30% and industrial sources contribute approximately 15%.[10]

Respirable particulates pose a greater health risk due to their ability to travel to the deepest part of the respiratory tract.[10,11] Schwartz *et al.* found that a 10 $\mu g/m^3$ increase in a two-day mean $PM_{2.5}$ was associated with a 1.5% (95% CI; 1.1% to 1.9%) increase in total daily mortality. Somewhat larger increases were found for deaths caused by chronic obstructive pulmonary disease (+3.3%).[3] These data suggested that increased daily mortality is specifically associated with particle mass constituents found in the aerodynamic size range under 2.5 μm, that is, with combustion-related particles.

The distribution and deposition of particles in the lung varies substantially with particle size. Coarse particles have a higher probability of being deposited in the bronchial region. Fine particles have a higher probability of being deposited in the periphery of the lung, especially in the respiratory bronchioles and alveoli, where their clearance is slow relative to particles deposited on airways.[3] Animal bioassay studies have been carried out in order to estimate the potential human risk associated with air particulate exposure. Prolonged exposures of rats to high levels of poorly soluble, non-fibrous particles, such as carbon black or diesel exhaust initiates a progression of cellular changes that eventually leads toward the development of lung tumors. Recent studies (between 1993 and 1997) have confirmed that it is the particulate matter that is primarily

responsible for the rat lung response to high concentrations of diesel exhaust and carbon black (primary particle diameters: 10-50 nm).[12,13]

People who live in highly industrial regions often inhale high levels of industrial emissions, including airborne dusts and products of incomplete combustion. In a health-related study in the Northeast area of Hamilton, a significant correlation was found between industrial air pollution and mortality rates for respiratory diseases, lung cancer and some other cancers.[14] Studies on cancer deaths in the late 1960's revealed the highest mortality rates closest to the main sources of industrial emissions in Hamilton.[14] In the 1970's, standardized lung cancer mortality ratios, which account for age, sex and smoking habits, were approximately 15% higher in the industrial area of Hamilton than in the residential area on the Hamilton escarpment.[15] Hospital admissions in Hamilton for acute respiratory disease were found to be associated with levels of air particulate in areas closest to the industry.[16] The Hamilton-Wentworth Air Quality Initiative (HAQI), which is a cooperative initiative of partners including government, industry, community and academia, reported that a substantial burden of illness and premature deaths is associated with air pollution in Hamilton-Wentworth. The estimated number of premature mortalities due to air pollution in Hamilton range from 90 to as high as 321 per year (1997 data).[10] The corresponding number of hospital admissions is estimated to be about 300 per year. In comparison, Ontario's smog plan (1996) has estimated a total of approximately 1800 premature mortalities and 1400 hospital admissions per year in all of Ontario due to the effects of inhalable particulate.[10] It should be recognized that these serious heath outcomes of hospital admissions and death are just the tip of the iceberg and that the pollutants

associated with air pollution lead to a number of other morbidity effects (e.g., chronic bronchitis, hospital emergency room visits, asthma symptoms, restricted activity days).

Public concerns regarding industrial air emissions are not unique to Hamilton. There are multitudes of large industrialized cities worldwide that share the same problem. There are common concerns regarding not only the filth resulting as a consequence of air particulate deposition, but also the public health effects resulting from it.

1.1.3. Pollutants of Concern

Any combustion process that does not reach completion will likely produce polycyclic aromatic compounds (PAC) as a byproduct. Some PAC are known to be human carcinogens.[17] While polycyclic aromatic compounds have been found routinely in studies of air particulate, several dozen inorganic elements have also been identified in similar studies. Many of these elements (in the form of compounds) are associated with the natural background aerosol, but certain species are for the most part due to anthropogenic activities.[2,4,18] Interest in the amounts, origin, and fate of certain inorganic species and PAC in urban air has increased primarily due to the deliterious health impacts that arise from human exposure to these pollutants.

1.2. POLYCYCLIC AROMATIC COMPOUNDS

Polycyclic aromatic compounds (PAC) are a class of organic compounds composed of benzene rings fused together on one or more sides. The chemical structures of a selection of PAC are shown in Appendix I. This class of compounds includes the homocyclic polycyclic aromatic hydrocarbons (PAH), and aromatic compounds containing heteroatoms such as sulfur (termed thia-arenes or PASH – polycyclic aromatic sulfur heterocycles), nitrogen (nitro-PAH and aza-arenes) and oxygen (oxy-PAH such as ethers, ketones, quinones, alcohols and phenols).

1.2.1. Sources of PAC in Air

Polycyclic aromatic compounds are ubiquitous in the urban atmosphere and were one of the first atmospheric pollutants to be identified as suspected carcinogens. PAC exist in the environment as complex mixtures containing many structural isomers and alkylated derivatives. They are derived as products from the incomplete combustion and pyrolysis of fossil fuels and other organic materials. PAC have been detected in pollutants such as carbon black and coal products, steel foundry emissions and particulate derived from diesel and gasoline-fuelled vehicles, power generation, incineration, residential heating, woodstoves and even barbeques.[19,20-22]

Levels of one PAC, benzo[a]pyrene (BaP), continue to exceed the Ontario ambient air quality criterion (AAQC) at several sites in Hamilton. The high levels of BaP in Hamilton appear to be associated with industrial activities since high levels of PAC are often correlated with samples collected downwind of the industrial zone.[10] Estimates of

atmospheric PAH emissions by source type have indicated that stationary sources accounted for 80 – 90% of the total PAH emissions.[23,24] Other research suggests that in urban and suburban areas, mobile sources are more likely to be the major PAH contributors.[25,26,4,22,27]

Among industrial sources, Potvin stated that the production of metallurgical coke is the single most significant source of ambient polycyclic aromatic hydrocarbons in Ontario.[9] In coal conversion and coking operations (as encountered in integrated steel mills), at temperatures between 400 to 750°C, the volatile products of the coal decomposition are released. As they pass through the hot coke, the volatile products form aromatic hydrocarbons, phenols and PAC.[28,29-31]

1.2.2. PAC in Air Particulate

PAC have been found routinely in air particulate extracts. An air particulate sample is collected by drawing air through a sampling device containing a filter and/or a solid sorbent. Particles are trapped by the filter while vapour-phase pollutants are trapped on the solid sorbent. Gas-particle partitioning of PAC is dependent on ambient temperature, particle age, meteorological conditions and sampling conditions.[29,32,33] The sampling and analysis of airborne PAC has recently been reviewed.[34,35]

The size of the particles that transport PAC in the air is also important. Smaller particles are the most dangerous, as they will more readily pass through emission control devices, remain suspended in the atmosphere for long periods, and will deposit in the innermost regions of the human respiratory tract when inhaled.[32] PAH are not uniformly

adsorbed over the entire particle size range. A number of studies have found that nearly 90% of PAC are on particles less than 3.3 μm in diameter.[27,36,37-39] The distribution of PAC on air particulate has been found to depend on particle size, source of PAC and volatility of PAC. [27,40,41,42] All studies reviewed indicate that the majority of the PAC are found on the low or sub-micron particle size range due to the larger surface area associated with these smaller particles.

1.2.3. Health and Environmental Impacts of PAC in Air Particulate

Concentrations of PAC in Hamilton air are in the same range as those in the air of New York City and Los Angeles, California.[36,43] The problem associated with Hamilton air particulate may be much more far reaching than Hamilton alone. Airborne pollutants may travel hundreds of miles, contaminating even remote environments. Studies of sediments in areas located near industries, have suggested that marine PAC contamination occurs by atmospheric deposition as well as from runoff and industrial effluents.[2,21,38,44] Extracts of Hamilton air particulate[25,26,45] and Hamilton Harbour sediment[37,46,47] have been found to be mutagenic. Most particulate-phase PAC are adsorbed onto particles from 0.2 to 2 microns in diameter; these small particles have large relative surface areas on which to bind. These particles only deposit slowly from the atmosphere and, depending on atmospheric conditions, may be airborne for days or even weeks, being transported over long distances.[48] PAC have been identified in the world's most remote parts.[27,49]

Toxicity of pollutants in the air is a major concern because humans receive direct exposure to the pollutants through inhalation, and indirectly through atmospheric deposition

on land and in water.[22,50] Steel foundry workers, smokers and people who live in highly industrialized regions often breathe in high levels of combustion products, including carcinogenic PAC. "Fingerprints" of this exposure were detected in worker's lung and blood cells, in the form of PAH-DNA adducts. [51] DNA-damaging complexes arise when such hydrocarbons bind to DNA.[51] In a study published by Gibson *et al.* it was concluded that lung cancer mortality amongst foundry workers at Dofasco, Ltd. was significantly higher than that found elsewhere in the plant or in a control population. Possible sources of carcinogens include metal fumes, dusts and pyrolysis products formed from the organic materials used as binders.[52] Improvements in the steel industries are currently being made in the areas of emission control technology, coke oven design and maintenance practices to reduce PAH emissions.[19]

1.3. METALS IN AIR PARTICULATE

1.3.1. Metals of Concern

Attempts to identify pollution sources using metals, or elemental compositions of air particulate, have involved inorganic analyses of ambient air samples. Elemental concentrations in air particulates by themselves are not sufficient to define the state of a polluted atmosphere or its effects on public health. The molecular state as well as the phase in which elemental pollutants is present may be of importance in terms of toxicity.[18]

Several dozen chemical elements have been identified in the atmospheres of urban and industrial basins.[4,27,49,53] Many elements including sodium, chlorine, silicon, and

aluminum are associated with the natural background aerosol, but certain exotic species including lead, zinc, and barium are for the most part due to anthropogenic activities.[2,4,27,49,54-56,57] Metals can enter the atmosphere from a wide variety of sources including fuel oil combustion, coke manufacture, iron, steel and cement manufacture and vehicular emissions.[58,59] Interest in the amounts, origin, and fate of certain elemental species has increased in recent years. Trace metals such as mercury, barium and lead are known to have implications for public health and ecology.

1.3.2. Health and Environmental Impacts of Metals in Air Particulate

Trace elements derived from coal burning sources, coke manufacture, fuel oil combustion, iron and steel manufacture, cement manufacture, and transportation sources have been identified.[60,28] The trace elements most commonly emitted from iron and steel operations are Fe, Mn, Cu, and Zn; coal, coke and fuel oil combustion are mainly responsible for As, Cr, Sn, Ti, Ni, and V emissions.[28,59]

Studies of industrial fly ash have found that Be, C, Ca, Cr, K, Li, Na, P, Pb, Si, Tl, V, and Zn are concentrated on the smallest particles.[28] Results from many studies indicate that the highest trace element concentrations occur in those smaller particles with high surface-to-mass ratios. HAQI identified metals such as cadmium, lead and manganese as priority air toxics for study in Hamilton. Cadmium is considered to be a carcinogen and can also induce kidney damage. Lead and manganese have adverse effects on the nervous system.[10,56] Chromium, arsenic, selenium, zinc and mercury are also known to be toxic.[55,56]

1.4. SOURCE APPORTIONMENT OF AIR PARTICULATE

1.4.1. Source Apportionment Strategies

There are many potential sources of air particulate in Hamilton. Airborne particulate may consist of wind-blown dust from industry, roads, dusts from construction sites and agricultural areas, ash from forest fires and vehicular exhausts. The analysis of air particulate can become very complex when there are a great number of potential sources contributing to the particulate levels in the air. The future expansion and development of air pollution control regulations requires an understanding of the origin of pollutants and the relative contribution of individual sources to ambient pollutant levels. In an urban center which has a large number of possible pollution sources, it is desirable to develop a source apportionment strategy in order to identify major air pollution sources, and quantify the contributions of pollutant species to each identified source. Many studies have been performed in the development of source apportionment strategies for ambient air.[18,21,43,61,62]

As a means of source apportionment, air pollution dispersion models have been developed in order to estimate ambient concentrations of specific pollutants.[63] In developing a dispersion model, emission rates of a specific pollution source are monitored and dispersion factors are taken into account in order to calculate theoretical concentrations of a pollutant at specific distances from the source. Traditionally, government agencies have used emission inventories as input for dispersion models that estimate ambient concentrations.[64,65] Dispersion modeling approaches are very useful but

may not adequately describe the complicated random nature of dispersion in the atmosphere and often do not include fugitive emissions or emissions from accidental events.[66] This modeling approach is only as good as the emissions inventory on which it is based. Emission inventories quickly become outdated as changes are made to fuel composition, emission controls and analytical technology.

Pollution source receptor models that use observed ambient pollutant concentrations to apportion the pollutants between several sources have also been developed. In these models, ambient concentrations of pollutants are monitored at the receptor, or sampling site, and these observations are used to calculate the contribution of individual sources. Receptor-oriented models have recently gained more interest because they do not require previous knowledge of the source emission profile. Receptor models are commonly used in conjunction with dispersion models to increase the reliability of source apportionment.[64] Our research group has employed the source-receptor technique in source apportionment studies using sulfur-containing polycyclic aromatic compounds.[62] In the present study, chemical data from source samples and receptor samples were used to characterize pollution sources.

1.4.2. Chemical Tracers

For decades, source apportionment strategies in ambient air applications were based solely upon the use of one type of chemical tracer, either organic compounds (primarily PAH or polychlorinated biphenyls (PCBs)) or inorganic compounds (primarily metals) as source indicators (or source tracers). In these strategies, each pollutant source was categorized and assessed for unique individual chemical source profiles or signature compounds associated primarily with one source category.[27]

If sources of pollutants contained unique tracer compounds, it would be possible to characterize pollution sources. Trace elements have been used to characterize sources, such as the use of lead as a tracer for gasoline emissions.[6,17,18,57] In recent years, interest in the individual organic and inorganic constituents of aerosols has grown, in part because of their potential for use as tracers in source apportionment models.[27] For source apportionment studies, it is desirable that each pollutant source provides an individual source profile fingerprint or signature.[17,6,18,27] Data sets are often complex, however, with certain source signatures being masked.[61,27]

1.4.3. PAH as Source Tracers

Levels of individual PAC and PAC ratios have been suggested and used as potential source apportionment tracers for ambient air analysis.[6,12,17,18,22,30,31,49,61,62,67-73] In early reports, individual PAC were identified in source samples and proposed as source indicators, however, it was soon realized that the majority of PAC were common to multiple sources. It was then recognized that although sources had common PAC, the

relative amounts of various isomers often differed. Patterns of PAC in several sources have been published as source inventories.[23,74,75] Variations in source profiles have been used to try to distinguish between different pollution sources. Ratios between specific PAC were examined and proposed as source tracers.[22,24,74] Problems including volatility, reactivity and source variability complicate this approach. Overall, the use of polycyclic aromatic hydrocarbons as pollution source tracers has not resulted in robust pollution source methods.

1.4.4. Difficulties with Source Apportionment using PAH

Certain source tracers are appropriate only when one major pollution source is present. In the earliest source apportionment studies, individual PAH were used as source tracers. Many of the same PAH are found in different pollution sources, making it difficult to distinguish these sources on the basis of PAH content.[6,62,72,76] For example, PAH such as phenanthrene, fluoranthene and pyrene have all been identified as source tracers not only for coal combustion, but also for incineration, wood combustion and petroleum-powered vehicles.[43] In addition, concentrations of coronene and benzo[ghi]perylene correlate with traffic emissions and have been used as source tracers to estimate traffic density.[6,17,18,61,72] This approach was found later to be useful only when traffic is the major pollution source due to the presence of coronene and benzo[ghi]perylene in coal and oil combustion emissions. In the case that an air particulate sample is collected at a location where emissions from more than one of these sources is likely, it would be impossible to determine the origin of the particulate collected using PAH source tracers

which are common to all potential sources. Often it is necessary to examine the whole profile of PAH.

Source profiles have been compared by normalizing each PAH concentration to the concentration of one standard PAH compound.[6,61,77] PAH concentrations are typically, but not exclusively, normalized to benzo[e]pyrene, a stable and relatively non-volatile PAH. This led to the investigation of several PAH ratios and some ratios were found to vary from source to source. Many of the ratios were found to be appropriate source tracers exclusively when only one PAH source was present.[32,68,70,71] Despite great variability in source profiles, ambient samples often appear similar.[67,78] Source samples have been used to determine characteristic PAH profiles in combustion emissions from motor vehicles, fuel oil, wood, coal and kerosene.[30,69] Air and sediment samples taken at different sampling sites in different seasons yield almost identical PAH profiles.[32,67,78,79]

Problems also exist with variability within a single pollution source type.[75,80] Coal used for residential heating was found to produce more PAH than coal used for coal-fired power plants.[81] Even temperature of combustion can cause PAH profile variability amongst a single pollution source. While low temperature combustion can favor the formation of alkylated PAH, high temperature combustion of fossil fuels favors the formation of unsubstituted aromatic compounds.[82-84] In addition, it is difficult to obtain a representative sample for source apportionment, especially from mobile pollution sources such as cars and trucks.

Reactivity or volatility of PAH may influence their utility as source tracers. Differences exist in the reactivities of various PAH compounds. The use of reactive PAH

in source apportionment studies may lead to inaccurate results. Cyclopenta[cd]pyrene has been identified as a tracer for vehicle emissions, but the utility of this compound in source apportionment studies is limited due its high reactivity.[67] Benzo[a]pyrene and benz[a]anthracene are also very reactive, and for this reason, many studies have eliminated these species from the analysis.[12,78,87,88] Traffic emissions are typically represented by air samples collected in tunnels.[61,62,69,70] These samples are not exposed to sunlight and may not be representative of ambient air. Humidity, temperature, sunlight and particle organic composition have been shown to influence the lifetime of PAH bound to air particulate.[85,86] The distribution of PAH between the particulate and vapour phases will also affect the PAH profile determined for air particulate. This distribution depends on ambient temperature, particle age, meteorological conditions and sampling conditions.[29,32,33,78,89]

1.4.4.1. Relevance of limitations to the current study

The use of chemical tracers for source apportionment purposes is rather complex. The work presented in this thesis was not intended to fully address each of the limitations discussed. We have attempted to minimize some of the aforementioned problems by taking the following measures in our study: (1) the presence of more than one pollution source was considered, (2) profile differences were evaluated in ambient samples and in source samples, (3) more than one sample of a single source type were analysed where possible to examine source variability, (4) efforts were made to obtain representative source samples, (5) volatility effects were minimized by choice of compounds used for source apportionment purposes.

1.4.5. Thia-Arenes as source apportionment tracers

Thia-arenes are polycyclic aromatic hydrocarbons that contain a sulfur atom in a thiophene ring. Structures and names for selected thia-arenes can be found in Appendix I. Thia-arenes are included in the larger classification of PAC or polycyclic aromtic compounds. In our research group, the use of thia-arenes as source tracers for diesel and coke oven emissions has yielded promising results. Thia-arenes (or PASH) are produced by fewer sources than PAH and as such, may be more effective source tracers than PAH. Thia-arenes are found in combustion products of sulfur-containing fuels such as coal and diesel fuel.

Thia-arenes have been identified in crude oils,[90-95] lubricating oils,[96] shale oils,[95,97,98] petroleum vacuum residue,[99] carbon black,[100-104] diesel exhaust particulate,[72,105,106] cigarette smoke,[107] coal and coal-derived products,[30,95,98,101,108-111] coal-fired residential stove emissions,[112,113] sediments,[114-117] marine organisms[116] and air particulate.[68,118,101,119] Thia-arenes were not detected in gasoline-fuelled automobile emissions[73,76] or emissions from the combustion of kerosene or wood.[30] Thia-arenes are, however, found at much lower levels in the environment (many are < 1% in abundance relative to the concentrations of major PAH).[23,38,69,70,88,120-123]

Allan *et al.* compared the thia-arene profiles in air particulate samples collected in Hamilton and Toronto, to the profiles in a selection of source samples.[62] Allan's results showed that thia-arenes are useful source tracers in distinguishing industrial coke oven emissions and diesel particulate emissions in ambient air particulate.[62] A few previous studies used thia-arenes as source tracers in sediments[124-127] and as indicators for the

maturity of crude oils.[97,128,129]

A particular type of thia-arene was evaluated as a source tracer for this study. Some major pollution sources studied in this thesis, including carbon black, coke oven emissions and diesel-powered vehicle emissions are expected to contain significant levels of thia-arenes due to the presence of sulfur in their petroleum feedstocks. Other sources of PAC that do not emit thia-arenes, such as gasoline exhaust, are not expected to interfere with the source apportionment model.

1.4.6. Organic and Inorganic Source Apportionment Tracers

Metals have been used as source tracers in various studies targeted to specific pollution sources. Often, when a particular industrial emission is known to have a characteristic inorganic signature, elemental analyses of samples taken at locations surrounding the potential source are carried out in a monitoring capacity. In source apportionment studies based upon the chemical element balance, it is assumed that each type of source (e.g., automobiles, metallurgical industries, incineration) emits a characteristic series of elements. The appearance of this set of elements in an air sample can be regarded as an indicator of pollution derived from a particular source. In a source apportionment study for carbonaceous aerosol in New York City, elemental tracers were used for auto exhaust emissions (Pb), residual oil/fuel oil combustion (V), resuspended road dust (Mn or Fe), and incineration (Cu or Zn).[130] Source tracers which have been used for resuspended soil are Si and Ti.[130]

Only in recent years have organic and inorganic species been used in combination as source tracers in source apportionment studies. In a 1996 study, Harrison *et al.* used PAH and inorganic species in a joint source apportionment exercise.[27] In this study, air particulate collected (PM_{10} and $PM_{2.1}$) on filters in Birmingham, UK was analysed for 18 PAH and 19 metal species. The authors were able to identify major air pollution source categories in an urban location, along with the quantitative contributions of pollutant species to each source category.[27] Results from this study demonstrated that a combination of measurements of PAH and inorganic pollutants may be a far more powerful tracer of emission sources than PAH data alone.

A source apportionment strategy conducted by Sexton *et al.* (1985) focussed on the contribution of residential wood combustion to measured ambient air particulate levels in Waterbury, Vermont.[77] This study also utilized both organic and inorganic species as source tracers. Sexton was able to identify elemental ratios indicative of residential wood combustion. Inorganic tracers known for crustal material (Fe and Mn), oil combustion (V and Ni) and other pollution sources were also monitored in the study. The PAH monitoring performed in this study indicated that local sources were primarily responsible for measured PAH values. In this case study, the use of inorganic species as source tracers yielded more valuable source apportionment information than did the use of PAH.

1.5. INDUSTRY IN THE CITY OF HAMILTON, ONTARIO

The City of Hamilton is one of the most heavily industrialized cities in Canada. Hamilton is located at the western end of Lake Ontario, harboring major industries as well as many other smaller industries and is bordered by two major highways (the QEW Niagara and Highway 403). Two major integrated steel manufacturing companies with coking operations are situated in the north end of the city on the southern shore of a large natural harbour (see Map 2.1). These steel mills and a carbon black company have been targeted as sources of pollution and black particulate in the east-end of Hamilton. Industrial emissions to the atmosphere can occur as stack emissions, process leaks and fugitive emissions. Fugitive emissions of industrial byproducts can originate from outdoor storage piles, industrial activities or accidental events. The industrial area is serviced by heavy traffic, particularly by large diesel-fuelled trucks.

1.5.1. The "Black Fallout" Issue

Industrial sites in Hamilton are in close proximity to Hamilton Harbour and several surrounding residential areas (see Map 2.1 for industrial locations). The fate of air particulate emissions from industrial sites in Hamilton is therefore a topic of great public concern. In Hamilton, residential areas at the north-east part of Hamilton bordering Hamilton Harbour, such as the Homeside community, the Woodward community and homes along the Beach Strip aside Lake Ontario all lie within a region of potential impact from atmospheric industrial emissions.

Residents of communities in the east-end of Hamilton have complained about

"black fallout" on their properties; this air particulate deposition takes the form of a fine, greasy black film that coats their houses, cars, outdoor furniture and swimming pools. Complaints of black fallout have increased in recent years and underline the importance of the study of air particulate and industrial pollution in Hamilton.

A carbon black company located in the east-end of Hamilton, named Columbian Chemicals Canada Ltd., has been suspected as the primary source of this black particulate. Columbian Chemicals has acknowledged that plant upsets have occurred in the past which have impacted residents in these areas. However, based on complaints from residents of other communities in the city which were unlikely to have been impacted by activities at the carbon black plant, it is clear that there are other sources of black particulate in Hamilton air. Sources of black particulate in Hamilton other than carbon black include emissions from steel industry sources such as coke ovens, blast furnaces, storage piles and vehicles together with dusts from roads and stone crushing. Exhaust emissions from vehicular traffic within the city and on neighboring highways are also potential sources of atmospheric particulate matter in the Hamilton. Some residences are located less than 240 meters from some of the coke oven batteries of the steel mills. As coke oven emissions consist of fumes and black particulates, the potential for black fallout particulate in these areas would be quite high as a result of this proximity. With all of these potential sources of black particulate, determination of the origin(s) of black fallout is extremely challenging.

One of the major problems that has faced the Ministry of the Environment (MOE) in dealing with public complaints regarding "black fallout" has been the lack of an analytical procedure that would allow laboratory staff to distinguish between carbon black and other types of "black fallout".

1.6. THE CARBON BLACK DILEMMA

Carbon black is an engineered material found in many items in daily use. The utility of carbon black in the reinforcement of elastomers accounts for most of its production. By far the greatest quantities of carbon blacks are used in rubber applications, particularly in automotive tires. About one-fourth of the weight of a standard automobile tire is carbon black.[131] Carbon blacks are used extensively in tire carcasses, belts, hoses and cable jackets. Carbon blacks are also employed to a lesser degree in printing inks and toners, paints and lacquers, plastics, ceramics, enamels and fibres, chemicals, paper, batteries, electrodes, videotapes and other miscellaneous applications.[132,133]

The production of carbon black in the United States alone exceeds 4 billion pounds per year. Columbian Chemicals, a Phelps Dodge subsidiary, operates carbon black plants in North America, Europe and Asia and is adding nearly 400 million pounds of new capacity to its global system through an expansion program which began in 1996. As the carbon black industry continues to grow, monitoring of carbon black emissions to the environment becomes all the more important.[134]

1.6.1. Carbon Black - What is it?

Carbon black is a black fluffy, extremely fine, odourless powder. It is composed essentially of elemental carbon obtained by partial combustion or thermal decomposition of hydrocarbons. Carbon blacks exist in the form of near-spherical particles of colloidal sizes, coalesced mainly into particle aggregates. Carbon blacks have particulate sizes in the respirable range. In this respect, they closely resemble diesel soot.[133]

Most types of carbon black contain over 97 – 99% elemental carbon. Carbon blacks may also contain chemically bound hydrogen, oxygen, nitrogen and sulfur. Because of their source materials, the methods of their production and their large surface areas and surface characteristics, commercial carbon blacks typically contain varying quantities of adsorbed by-products from the production processes, particularly aromatic compounds. Typical classes of chemicals adsorbed onto the carbon black surface are polycyclic aromatic hydrocarbons and sulfur-containing PAH (thia-arenes).[135] The presence of these compounds can significantly increase the hazards of carbon black exposure.[13,136]

1.6.2. Microstructure of Carbon Blacks

Average particle diameters in commercially-produced carbon blacks range from 0.01 to 0.4 micrometers, while average aggregate diameters range from 0.1 to 0.8 μm. The microstructure of the carbon black particle may be visualized as a statistical ensemble of carbon layer planes, having different degrees of order. Not unlike graphite, the carbon black particle is composed of parallel layer planes of carbon, however, curved planes and various other distortions and imperfections are seen in its microstructure. In

the bulk of the particles layer planes seem to be vaguely oriented around a variety of centres randomly distributed in the particle, which could appear as "growth centres," apparently independent of the surface orientation.[132] Different types of carbon blacks show different degrees of order. This order is directly measurable by electron micrography as well as by x-ray diffraction.[133]

1.6.3. Organic Analyses of Carbon Black

Carbon blacks can contain relatively large quantities of extractable organic compounds, usually dark-colored oily materials. The nature of these extractables has been studied by means of gas chromatography-mass spectrometry (GC-MS) of organic extracts of carbon black.[135] The dominant chemical characteristic appears to be that of fused ring aromatics. Species have been identified with molecular weights up to about 650 Da. These compounds are most likely byproducts and not intermediates in the process of carbon black formation. Non-aromatic compounds are present in lesser amounts such as alkenes, dienes and other related compounds.

Carbon blacks have an unusual selection of polycyclic aromatic compounds (PAC) adsorbed to their surfaces, compared to the PAC commonly found adsorbed to diesel soot and urban air particulate.[102,137,100,135,138] The PAC found in carbon black extracts are comprised of mainly higher molecular weight, highly condensed species, while extracts of diesel particulate and urban air particulate contain PAC of a wide range of structural types and molecular weights. Carbon blacks have a very strong affinity for adsorbed polycyclic aromatic compounds and this affinity increases with the size of the

compound.[138] Therefore, compounds with high boiling points, low vapor pressures and large aromatic π-systems are adsorbed most strongly to carbon black particulate. Due to the strength of these adsorptions, aromatic solvents such as benzene, chlorobenzene and naphthalene have been required to extract high molecular weight PAC from carbon black.[137]

It was found in a study by Lee and Hites[102] that the amounts and structures of PAC associated with carbon blacks are quite dependant on the conditions of carbon black formation, including furnace temperature and the nature of the feedstock. Sulfur compounds are absent in carbon blacks produced from natural gas, but are present in all other carbon blacks produced from sulfur-containing feedstocks like coal.[139] This observation indicated that organic sulfur persists in the combustion of sulfur-containing petroleum feedstocks and appears as stable sulfur-substituted polycyclic compounds associated with carbon black products.

In the extraction of carbon black, methods using Soxhlet apparatus with various solvents have been employed. In addition, extraction methods using vacuum sublimation and ultrasonic extraction have been performed.[138] A significant variance in the extraction efficiencies of different solvents has been reported. Stenberg *et al.* stated that a dominant factor that influences the extraction of a component is the π-electron system, and that the strength of the interaction between the matrix and the component to be extracted is dependent on aromaticity.[138]

Comparisons of solvent extraction efficiencies in the extraction of carbon black have been investigated for polar solvents such as acetone and methanol, non-polar

solvents such as cyclohexane and dichloromethane, in addition to aromatic solvents such as benzene, chlorobenzene, toluene and naphthalene. Comparatively low yields were obtained using cyclohexane and methanol. Cyclohexane was found to be inefficient in the extraction of compounds of molecular weight 226 Da and higher. Methanol seemed to be too polar a solvent since the extraction yields were low for both PAH and oxygenated derivatives. Overall, of the non-aromatic solvents, dichloromethane exhibited the highest extraction efficiency for the majority of PAH.[138,140]

The best extraction yields for high molecular weight PAC were found using the aromatic solvents. This relatively high efficiency is probably due to the aromatic solvents' ability to overcome the interactions between the large aromatic π-systems of the PAC and the carbon black surface. Of the aromatic solvents, naphthalene is the most difficult to work with as it requires modified Soxhlet apparatus to maintain the solvent in the liquid state.[137] Lower molecular weight PAH have been found to be partially lost during the distillation of naphthalene.[137] Overall, toluene and chlorobenzene have been found to be efficient in extracting the widest range of molecular weights of PAC and are now the most commonly used solvents in carbon black extractions.

1.6.4. The Problems with the Identification of Carbon Black in Ambient Air

Prior to the research described herein, there were no chemical methods for determining ambient levels of carbon black in air. The MOE and Columbian Chemicals have used physical methods, primarily electron microscopy (EM), to examine individual particles in attempts to differentiate carbon black particles from other particles. Several

problems are inherent in the use of physical methods for carbon black identification and differentiation. A great deal of effort is required in order to examine a sufficiently large number of particles from one sample to make a statistically meaningful statement about that sample. Sampling artifacts can be troubling; that is, the specific particles examined may not be truly representative of the entire sample, but may be just a subset of the entire sample. In addition, analytical techniques based upon sample morphology, such as optical and transmission electron microscopy, have been shown to be unsuitable for distinguishing carbon black from diesel soot.[133] Therefore, as diesel soot is ubiquitous in urban atmospheres, microscopy techniques are not appropriate for this purpose.

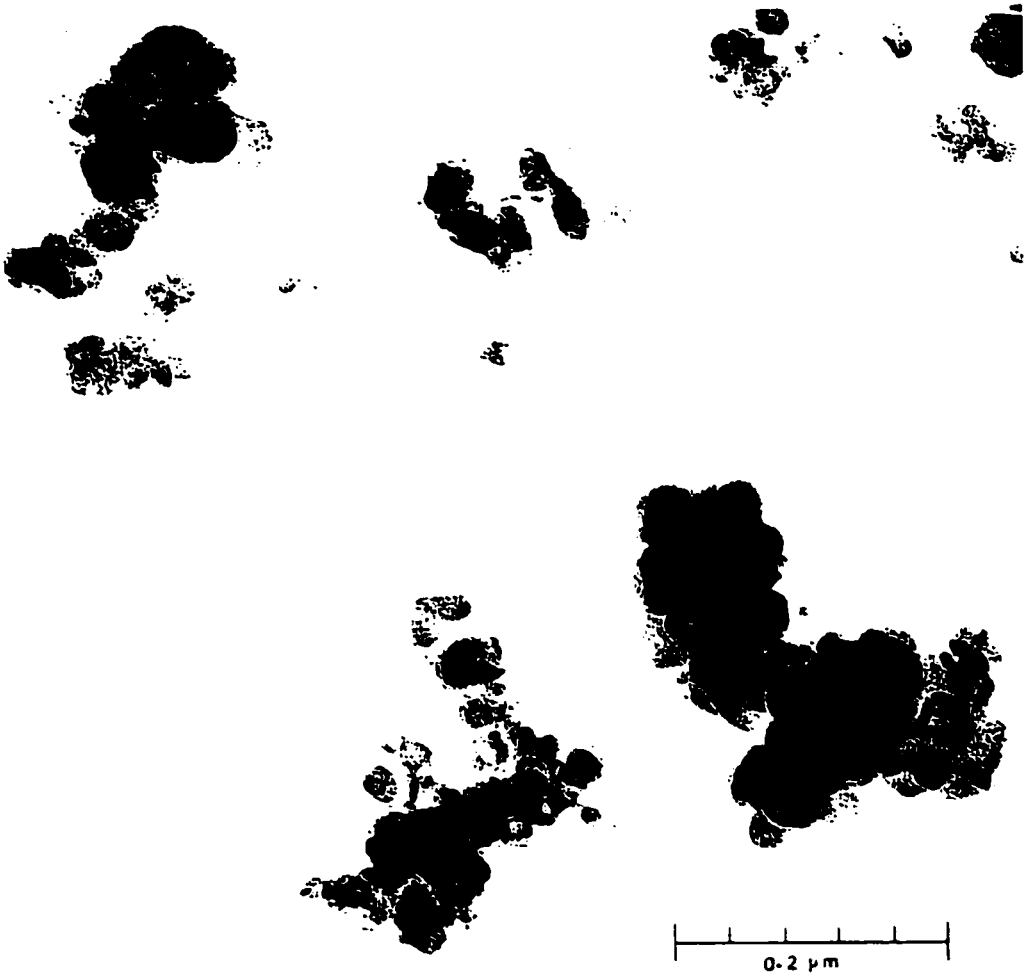
Other researchers have also not been able to differentiate diesel soot and carbon black. In a study conducted by Medalia *et al.*, samples of carbon blacks, chimney soot, soots from oil furnaces, oil and coal boilers and power plants were compared using an analysis scheme including the following methods: (a) qualitative inspection; (b) microscopic examination (light microscope and transmission electron microscopy (TEM); (c) measurement of selected physical properties; (d) determination of fraction of organic extractables; (e) determination of moisture, ash, weight loss by thermal gravimetric analysis (TGA) and elemental composition; and (f) determination of colloidal carbon content.[133] The only results which indicated that diesel soot could be distinguished from carbon black were based upon techniques comparing the fraction of organic extractables obtained from the samples and upon the hydrogen/carbon ratio obtained from elemental analyses of the samples. These techniques are only applicable if bulk samples of diesel exhaust and carbon black are analysed, which is not the case in ambient air analyses

where there may be only a few milligrams of these materials on a filter sample. Differentiation of carbon black and diesel soot could not be achieved by all other methods investigated.

It has been found that carbon black is composed almost entirely of "aciniform carbon", a term proposed by Medalia *et al.*[133] Aciniform carbon is a term which describes particulate carbon composed of spheroidal particles fused together in aggregates of colloidal dimensions. Aciniform carbon can be detected in a sample by transmission electron microscopy (TEM). Figure 1.1 shows typical aggregates of aciniform carbon in a carbon black sample. Soots from diesel engines also consist largely of aciniform carbon. Results from transmission electron microscopy showed that both carbon black and diesel soot consist largely of aciniform carbon and cannot be distinguished based upon morphology.[133]

Without a scientific approach to the problem, it is impossible to determine accurately the nature and source of the black fallout in Hamilton air particulate, especially in consideration of the many possible anthropogenic sources of particulate in the area. It is desirable not only to identify the source or sources of the particulate, but also to quantify the levels of particulate from each identified source. Attempts at air particulate analysis and differentiation by way of optical or electron microscopy have yielded unpromising results. The frustrations of the public, and those of the Ministry of the Environment have intensified the need for a source apportionment methodology for carbon black in ambient air.

Figure 1.1: Microstructure of carbon black N330 (TEM)[133]



1.7. FOCUS OF RESEARCH

Prior to the research described herein, there was no methodology available to identify and quantify carbon black in ambient air samples. Our focus has been to develop a new analytical method that would allow carbon black and other types of black particulate to be distinguished in ambient air samples. In 1995, the Ontario Ministry of the Environment (MOE) provided our research group with a grant for the development of a method to determine the levels of carbon black in ambient air. In 1997, Columbian Chemicals Canada Ltd. embarked on a major capital renovation program to improve the environmental performance of its carbon black plant on Parkdale Ave. N. in Hamilton. These improvements were designed to produce significant reductions in the numbers of plant upsets and in the amounts of carbon black and other chemicals released from the plant. In order to demonstrate that the planned capital expenditures had resulted in improved environmental performance of the plant, we proposed to provide a new methodology to detect ambient carbon black and to develop a program to monitor ambient air quality at locations within the communities near the plant. Columbian Chemicals Canada Ltd. accepted our proposal and has since funded the current research and the carbon black research beyond this thesis.

1.7.1. The use of PAC and Metals in the Source Apportionment of "Black Fall-out"

In the present research, polycyclic aromatic compounds (PAC) and inorganic pollutants are proposed for use in combination as tracers in source apportionment. In this

study, airborne particulate matter was collected at sites upwind and downwind of a carbon black plant and two steel mills. In addition, industrial source samples from two steel foundries and a carbon black plant were analysed. Through organic and inorganic analyses of these air and source samples, the source apportionment of black fallout in Hamilton was investigated.

1.7.2. OBJECTIVES

The main objectives of this research have been the following:

- To collect air particulate samples in the City of Hamilton which encompass urban air particulate contributions and industrial contributions to "black fallout" including those from steel foundries and a carbon black production plant.
- To develop a robust method for the identification and quantification of carbon black in ambient air samples.
- To apply this methodology to the monitoring of ambient air samples suspected of containing carbon black.
- To evaluate the potential of using metals as pollution source tracers in the source apportionment of black fallout in an industrial-urban setting.
- To make the data we obtain and the conclusions we reach during the course of this research freely available to Columbian Chemicals Canada Ltd., to the MOE, to community representatives and to the Hamilton Air Quality Stakeholders Committee.

2. SAMPLES

2.1. CHAPTER OVERVIEW

The City of Hamilton is a very complex environment and the siting of Columbian Chemicals provided unique challenges in terms of potential source contributions. Although Columbian Chemicals Canada Ltd. has been suspected as a principal source of black fallout in Hamilton, there are many other potential sources of black particulate including industrial processes, road dusts and vehicular exhaust. We set out to examine a large selection of air samples and industrial source samples in the development of an analytical methodology designed to distinguish between carbon black and other types of black particulate.

Using samples of carbon blacks from Columbian Chemicals, and ambient air samples collected upwind and downwind of the plant, we set out to develop the first method to determine carbon black in ambient air. Twenty-four hour air samples were selected for analysis by careful examination of hourly wind direction data in order to minimize potential interferences from the steel industry emissions. In order to assess the robustness of our method, potential interferences due to steel industry and vehicular emissions were evaluated. These source samples included steel industry samples, vehicular emissions, coke oven emission samples and road dusts. Organic and inorganic chemical signatures for these samples were determined in order to investigate a source apportionment method for "black fallout."

2.1.1. Samples for Analysis

There are four main categories of samples involved in this research: ambient air samples, industrial source samples, residential dust samples and reference material samples. The air samples include samples collected upwind and downwind of Columbian Chemicals and the steel industry coke ovens. Vehicular emissions were assessed by examining samples collected in 1994 along Hwy 404. The industrial source samples include coals and cokes, baghouse dusts, slags, coal tar and industrial road dusts. The residential dust samples were collected at residential homes in Hamilton in response to complaints by residents. These samples were collected from window sills, clothes lines and porches; some were collected from surface water at the shoreline of Lake Ontario. The reference samples consist of various NIST certified reference materials, coke oven condensate and diesel exhaust particulate samples. A detailed list of the samples involved in this research can be found in Appendix II of this document. A description of the sample preparation and analysis procedures used can be found in the methods section of Appendix III.

From four years of air monitoring campaigns (1995 – 1998), a total of 91 respirable air particulate filters were selected for extraction and PAC analysis. Each air filter underwent sequential extraction with dichloromethane for 24 hours followed by toluene for another 24 hours, providing a total of 182 sample extracts. A former graduate student, Laurie Allan, provided nine dichloromethane extracts for analysis. Lisa Heydorn provided ten dichloromethane extracts from air particulate samples collected in 1996.

The author performed the extractions, two-stage chromatographic cleanups, PAC analyses and thia-arene quantification of the remaining 163 samples. In addition, a total of 36 source samples were selected for extraction and PAC analyis. Each source sample also underwent sequential extraction with dichloromethane then toluene, providing 72 sample extracts. Many similar extractions and analyses were required for the development of the carbon black method.

2.2. AIR PARTICULATE SAMPLE COLLECTION

2.2.1. Air Sampling Stations

Our strategy involved simultaneous sampling of air particulate at sites located upwind and downwind of Columbian Chemicals Canada Ltd. The air samplers were sited in locations appropriate for the monitoring of fugitive emissions of carbon black from the plant. The net difference between upwind and downwind samples would be taken as the net impact at the downwind site. Air particulate samples were collected in 1995, 1996, 1997 and 1998 for this research as well as for other research projects. Twenty-four hour PM_{10} air particulate samples were collected during intensive air sampling campaigns during the periods of July 10 to August 20, 1995, April 5 to May 26, 1996, Sept. 2 to Oct. 8, 1997, and May 8 to July 10, 1998.

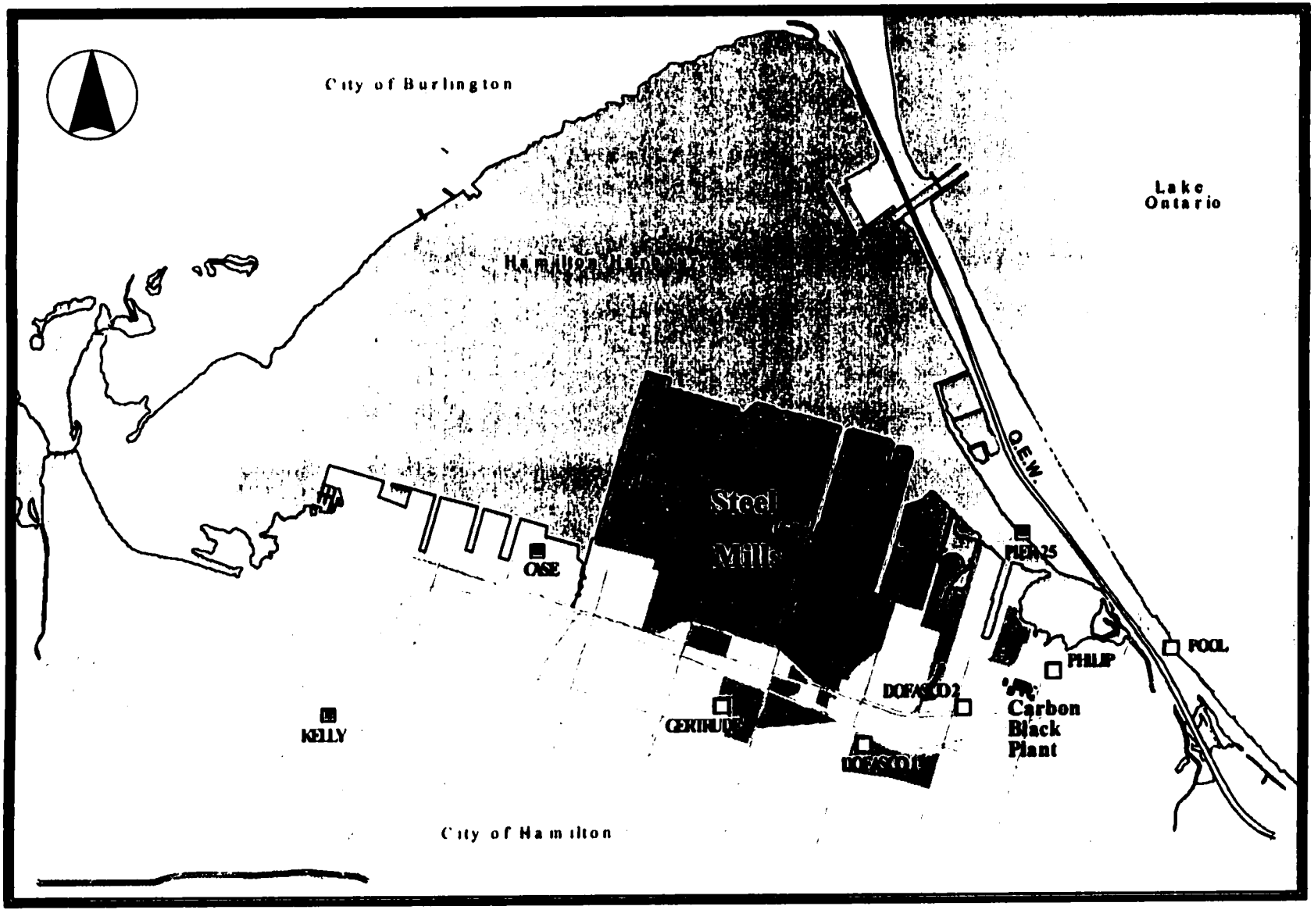
The air particulate sampling sites in the City of Hamilton used in this thesis research are shown in Map 2.1. The prevailing winds in Hamilton are from the west and the

southwest (approximately 45% of the time) and from the east and northeast (15% of the time); winds are calm about 25% of the year.

During the summer of 1995, six PM_{10} air samplers (air samplers described in section 2.2.2) were sited at six locations (named Kelly, Case, Pier 25, Gertrude, Beach and Philip) such that air particulate could be collected at locations upwind and downwind of the main industrial area simultaneously. Station 29000 (which will be referred to as "Kelly") is an Ontario Ministry of the Environment (MOE) air monitoring station just east of downtown Hamilton. Station 29113 (Gertrude), station 29547 (Pier 25) and station 29102 (Beach) were also established MOE air monitoring stations. These sites were secure, easy to access and provided protection for sample integrity. Stations 29531 (J.I. Case) and 29557 (Philip) were sampling sites established by our group. At the Case site a PM_{10} sampler was located on the roof of a three-storey Hamilton Harbour Commission building near the end of Hillyard St. The Philip site was located on the roof of a one-storey building which served as a weigh station for a scrap metal recycling plant on the Philip Services Corp. property.

In the 1995 air sampling campaign, the Philip site was chosen as the main downwind site for monitoring Columbian Chemicals because of its close proximity to the carbon black plant (300 m). The Gertrude site was chosen as the upwind counterpart, located on the corner of Gertrude St. and Depew St. in Hamilton, (approx. 2.8 km west of the carbon black plant).

Map 2.1: Air sampling sites - Hamilton, Ontario.



Inhalable air particulate (PM_{10}) samples were collected daily for six weeks from July 10 to August 20, 1995 at Stations 29000, 29113, 29557, and 29547, and from July 20th to August 20th, 1995 at Station 29531. The sampler at Station 29102 was shared with the MOE so samples were collected for four sequential days, followed by two days off, from July 10th to August 20th, 1995. A total of 219 respirable air particulate filters were obtained. Half of these samples was collected by the author and the other half by L.M. Allan.

Ambient air sampling was also conducted for 51 days in the spring of 1996 at the Pier 25 site as a part of another study. The Pier 25 site was chosen due to its proximity to the steel mills, and its location downwind of the coke ovens. These samples were used in this study to examine the potential contributions and interferences posed by coke oven impacts.

Different air sampling sites were established for the 1997 and 1998 air sampling campaigns. A site located approximately 1.4 km due east of Columbian on the shore of Lake Ontario at Lakeland Pool was designated as the Pool site. Two locations on Dofasco Inc. property were used as air sampling locations; the "Dofasco 1" site was used in 1997 and is located on the roof of a storage building near the corner of Kenilworth St. and Beach Blvd. approximately 1.5 km west of the carbon black plant. The "Dofasco 2" site was used in 1998 and was selected because it was even closer to the Columbian plant and is located near the corner of Burlington St. and Strathearne St. (approximately 0.6 km from the carbon black plant). Since the Dofasco 2 site was closer to the carbon black plant than the pool site, potentially larger carbon black impacts were expected at the Dofasco 2

site. These sites are identified on Map 2.1. The air samples in 1997 and 1998 were collected at two sites by Columbian Chemicals staff working in cooperation with our study.

Table 2.1: Summary of air particulate samples collected

Year	Number of Samples Collected
1995	219
1996	51
1997	50
1998	91

2.2.2. Air Sampling Methods

Inhalable airborne particulate was collected using an Anderson PM_{10} high volume air sampler (General Metal Works Ltd., Village of Cleves, OH) equipped with a flow controller operating at a flow rate of 40 ft^3/min. Flow controllers were calibrated before the sampling period and every two weeks during the sampling period. Timers were used to start sample collection at 8:00 a.m. on the sampling date and to stop sample collection at 6:00 a.m. the following morning. Filters were changed between 6:00 a.m. and 8:00 a.m. every day during the sampling period.

Air particulate was collected on Teflon-coated glass fibre filters (Pallflex 8x10 inch, type TX40H120WW, Pallflex Products Corporation, Putnam, Conn.). Filters were weighed on an analytical balance before and after sample collection. Filters were stored in a dessicator over a dessicant (Indicating Drierite; W.A. Hammond Drierite) for five days before weighing to reduce moisture content. After weighing, air filters were stored in their

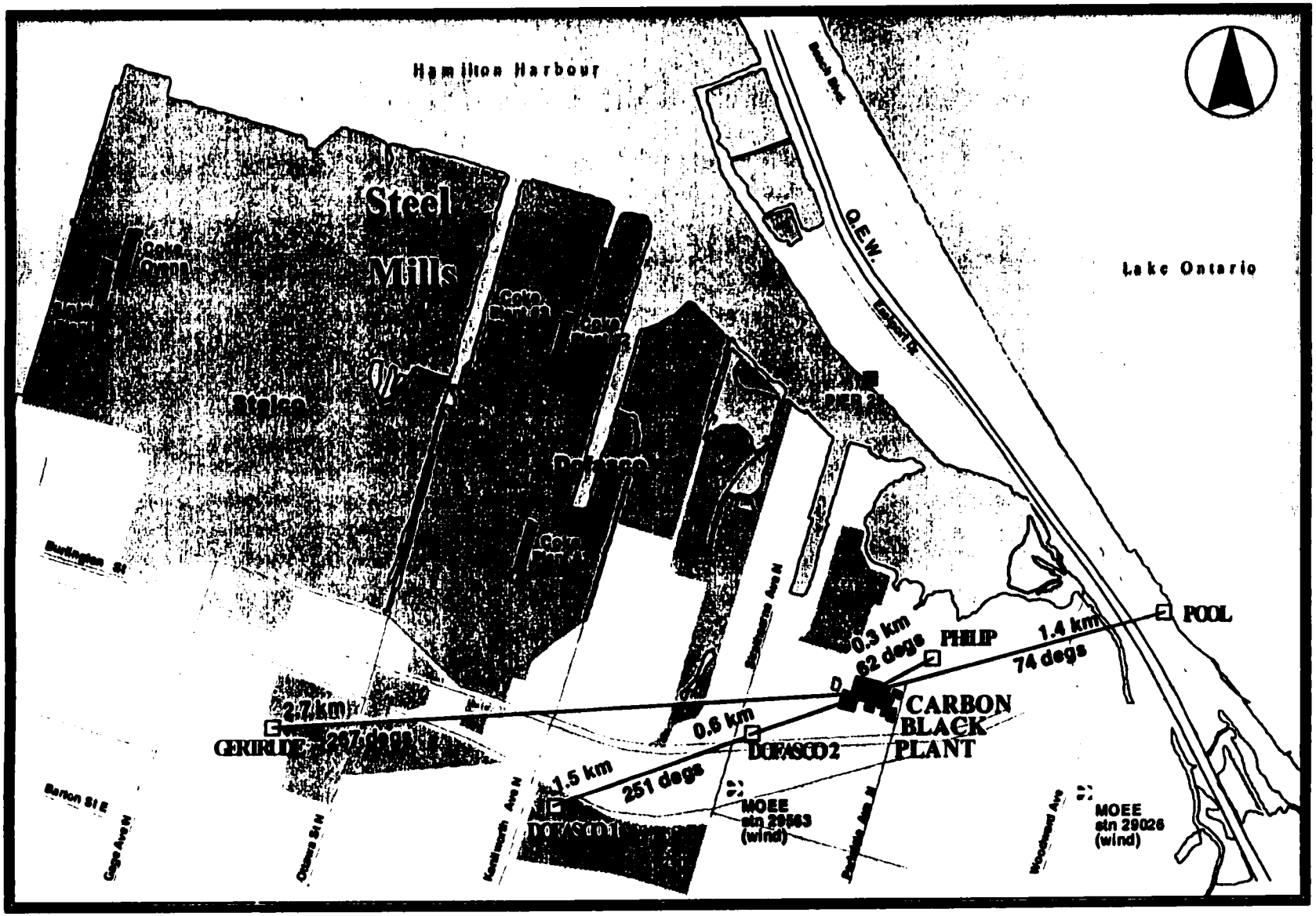
envelopes in a sealed bag (i.e., a zip-lock bag) in a freezer (-20 degrees Celsius). The air samples were collected with a sample volume normally within 1400-1700 cubic meters collected in a 22-24 hour sampling period (see air sample data in Appendix IV).

2.2.3. Meteorological Data: Selection of Air Samples for Analysis

The Ministry of the Environment provided hourly wind direction and wind speed data from a nearby meteorological site at the Hamilton Sewage Treatment Plant (Station 29026, Map 2.2). Using these wind data, we selected upwind/downwind sample pairs for analysis based upon the following selection criteria:

1. Average hourly wind directions should be such that the two sampling sites are upwind (within 15° of the direction opposite to the source) and downwind (within 15° of the direction of the source) for a substantial part of the sampling period (>7 hours of collection).
2. Average wind directions (over the sampling period) should have a narrow standard deviation (<45°; i.e., a relatively constant wind direction).
3. Most of the hours in the collection period should have wind speeds above 3 km/hr. (periods with very low wind speeds cannot be relied upon to provide useful samples because wind direction information is no longer meaningful).
4. Collection periods which had wind directions that could result in significant impacts from steel mill coke ovens were rejected.

Map 2.2: Distances and directions from carbon black plant to air sampling sites.



5. A wind direction reversal during the sample collection period (as often happens due to the effect of Lake Ontario) would render air samples inappropriate for our purposes.

Details regarding the wind data related to the sampling dates chosen for analysis are provided in charts in Appendix IV.

2.3. RESIDENTIAL DUST SAMPLING

Residential dust samples were collected primarily by Columbian Chemicals staff in response to complaints from local residents. These samples were provided to us in many different forms: dusts collected in jars, dust swipes on Kim-Wipe tissues from window sills and a clothes line, and suspensions of dusts in water from Lake Ontario. The samples were weighed, extracted and analysed in the same manner as was performed on air particulate samples.

2.4. SOURCE SAMPLES

2.4.1. Industrial Samples

We were provided with 60 source samples from industries including Columbian Chemicals Canada Ltd., Dofasco Inc. and Stelco Inc. and from the MOE. The source samples originating from the steel industries were categorized in the following manner: (i) coals and cokes (6 samples), (ii) baghouse dusts (10 samples), (iii) process samples derived from outdoor storage piles (2 samples), (iv) slags (5 samples), (v) miscellaneous process samples (11 samples), and (vi) dusts derived from roads surrounding the

industries (16 samples). Samples that are probable sources of air pollution, particularly baghouse dusts and process samples derived from storage piles, were made a priority for organic analysis.

This selection of source samples provided us with an advantage in this source apportionment research because these source samples originated from the actual industrial sites we were monitoring, as opposed to generic samples commonly used as pollution source references. As a result, we can be confident that the source tracer compounds identified in those source samples for source apportionment purposes were valid and applicable to the analysis of ambient air samples taken near the industrial sites. In addition, having such a large number of source samples in our possession provided us with a perspective of the potential types of particulate contributing to the ambient air samples.

2.4.2. Vehicular Emissions Samples

Air samples were collected at the fence lines on the east and west sides of Highway 404 in Toronto, Ontario in 1994 as part of another study. The site on the west side was on the grounds of Highland Memorial Gardens Cemetery while the other site was on the east side on Gordon Baker Road in a light industrial area. Samples were collected by workers from Rowan, Williams, Davies and Irwin, who were subcontracted by the Ontario Ministry of Transport. Seven filters from the Gordon Baker Road sampling station (see Table 2.2) were selected for analysis.

Table 2.2: Highway 404 air samples

Filter #	Date Collected	Mass Particulate Collected (g)
125	7/15/94	0.038
119	7/9/94	0.048
153	8/3/94	0.049
146	7/28/94	0.035
253	8/16/94	0.051
219	7/1/94	0.054
248	6/18/94	0.061

We obtained several diesel exhaust particulate samples collected by Environment Canada between May and July of 1998 from Dr. Chung Chiu of Environment Canada in Ottawa. The emissions from one vehicle, an Astro Van, were collected on Pallflex filters (Pallflex T60A20). The vehicle ran on a commercially available low-sulfur diesel fuel. The vehicle was run under different types of driving cycles. Each test cycle was repeated three times daily to provide 3 sampling replicates per driving cycle. The different driving cycles used for particulate sampling were as follows:

CBD Cycle: The "central business district" cycle simulated the duty cycle that of an urban transit bus full of people as it moves through the central business district of a city from bus stop to bus stop. A large part of this test cycle was spent idling. Two replicate filters were extracted together for PAC analysis (filter #: particulate weight - S19980619D91105C1: 4.82 mg, S19980619D91105C2: 4.55 mg).

WVU Cycle: The "West Virginia University" cycle simulated a sequence of idling, acceleration to a constant cruising speed, and deceleration to idle again. Each constant cruise speed was at a different speed, increasing from 20-40 mph. Two replicate filters were extracted together for PAC analysis (filter #: particulate weight - S19980707D91105W1: 6.88 mg, S19980707D91105W2: 6.63 mg).

SHE Cycle: The "Sheila" cycle is the last half of what is called the "New York City bus cycle" which includes accelerations and decelerations about a reasonably high speed (40 - 50 mph). Two replicate filters were extracted together for PAC analysis (filter #: particulate weight - S19980708D91105X1: 3.66 mg, S19980708D91105X2: 3.59 mg).

STE Cycle: (cycle description not given)

Two replicate filters were extracted together for PAC analysis (filter #: particulate weight - S19980506D91105s1: 2.85 mg, S19980506D91105S2: 2.28 mg).

2.5. STANDARD REFERENCE MATERIALS

In addition to ambient air samples, we examined NIST Standard Reference Materials SRM 1649 (urban dust reference) and SRM 1650 (diesel particulate reference) which were obtained from the National Institute of Standards and Technology (Gaithersburg, MD). Each sample was extracted and analysed using the procedures and instrumentation outlined in the experimental section of Appendix III.

3. DEVELOPMENT OF A METHOD TO DETERMINE CARBON BLACK IN AMBIENT AIR

3.1. CHAPTER OVERVIEW

In response to the need for a method to detect carbon black in ambient air, a sensitive procedure for the quantification of carbon black in air particulate has been developed. Until the present research, there have been neither standard nor quantitative methods for determining ambient levels of carbon black in air.

Our approach is based upon a sequential extraction methodology and the quantification of an unusual sulfur-containing PAC we have found on carbon blacks. This unusual sulfur-containing PAC was identified as benzo[6,7]perylo[1,12-bcd]thiophene (thiacoronene). Using thiacoronene as a source tracer for carbon black, we have been able to identify and quantify carbon black in ambient air samples collected downwind of a carbon black plant.

3.2. EXTRACTION AND ANALYSIS OF CARBON BLACK

3.2.1. Carbon Black

Most carbon blacks contain organic compounds at low levels which can be extracted with organic solvents. Thermal and furnace blacks generally contain relatively large quantities of extractables, usually dark-colored, oily materials. The chemical nature of these extractables has been studied using gas chromatograpy with flame ionization

detection,[138] and GC-MS[102,137] and using HPLC with UV detection.[141] The dominant chemical species are fused-ring aromatics, or polycyclic aromatic compounds, with molecular masses ranging from 128 to about 650 Da. These compounds are most likely byproducts and not intermediates in the process of carbon black formation. Nonaromatic compounds, present in lesser amounts, were identified as alkenes, dienes and related compounds. Based on this, we expected that carbon blacks would contain strongly adsorbed, high-mass PAC that could be used as potential source tracers for carbon black.

Polycyclic aromatic compounds have been extracted from carbon black samples using a variety of organic solvents.[100,102,138,137] Carbon blacks have very strong affinities for PAC and the adsorption strength increases with the mass and aromaticity of the compound.[138] Compounds with high boiling points, low vapor pressures and large aromatic π-bonding systems are adsorbed most strongly to carbon black particulate. Organic solvents with aromatic character such as benzene, chlorobenzenes and naphthalene have been used to extract PAC from carbon black.[137] In contrast, extraction protocols for ambient air particulate samples commonly employ a 24-hour Soxhlet extraction using dichloromethane as the extracting solvent. Anticipating our application to ambient air samples, we proposed to use a dichloromethane extraction for ambient carbon black analysis followed by a subsequent extraction with toluene, an aromatic solvent. Toluene was chosen with the expectation that it would extract the more strongly adsorbed organic compounds from carbon black that would probably not be removed in the initial dichloromethane extraction. Toluene is a relatively safe solvent to work with in the laboratory as compared to benzene, chlorobenzene and naphthalene. The

development of this new sequential extraction method is described later in this chapter in Section 3.5.

3.2.2. *Preliminary Analyses of Carbon Black*

Columbian Chemicals Canada Ltd. has a carbon black plant based in Hamilton Ontario. Columbian produces over 12 different types of carbon black targeted for different end uses. In preliminary analyses we extracted carbon black N330 using 3 sample replicates and analysed the extract using normal phase preparative HPLC and GC-MS. The PAC in carbon black N330 were identified by HPLC with diode-array detection (see Figure 3.1) using the library of UV spectra of PAH standards contained in our database (see Table 3.1). A compound that eluted just prior to pyrene was identified as phenanthro[4,5-bcd]thiophene (208 Da; see structure in Appendix I) by comparison to an authentic standard. One compound could not be identified by this spectral matching method. This compound was also proposed, but not identified in literature reports.[137] The GC-MS total ion chromatogram of carbon black N330 extract is shown in Figure 3.2. The dominant PAC in carbon black N330 were pyrene (150 μg/g), coronene (64 μg/g), benzo[ghi]perylene (37 μg/g), benzo[ghi]fluoranthene (21 μg/g) and an unidentified compound which eluted near benzo[ghi]perylene and coronene. The amounts of all PAC identified are listed in Table 3.1 and totalled 320 μg per gram of carbon black.

Table 3.1: Summary of concentrations* of polycyclic aromatic compounds (PAC) in carbon black N330.

Compound in Carbon Black N330	MW (Da)	Concentration in Toluene Extract (μg/g particulate)*
Fluoranthene	202	15 ± 0.9
Phenanthro[4,5-bcd]thiophene	208	7.0 ± 0.2
Pyrene	202	150 ± 9
Benzo[ghi]fluoranthene	226	21 ± 1
Cyclopenta[cd]pyrene	226	7.7 ± 2
Chrysene	228	< 0.001
Benzo[b]fluoranthene	252	0.11 ± 0.01
Benzo[k]fluoranthene	252	< 0.001
Benzo[j]fluoranthene	252	< 0.001
Benzo[e]pyrene	252	1.7 ± 0.1
Benzo[a]pyrene	252	0.93 ± 0.3
Perylene	252	0.08 ± 0.01
Indeno[1,2,3-cd]pyrene	276	2.1 ± 0.2
Dibenz[a,c]anthracene	278	< 0.001
Benzo[ghi]perylene	276	37 ± 3
Unidentified Compound	306	18 ± 0.8
Coronene	300	64 ± 2
Total PAC Value =		320 ± 20

* these concentrations were calculated from analyses of 3 replicate extractions

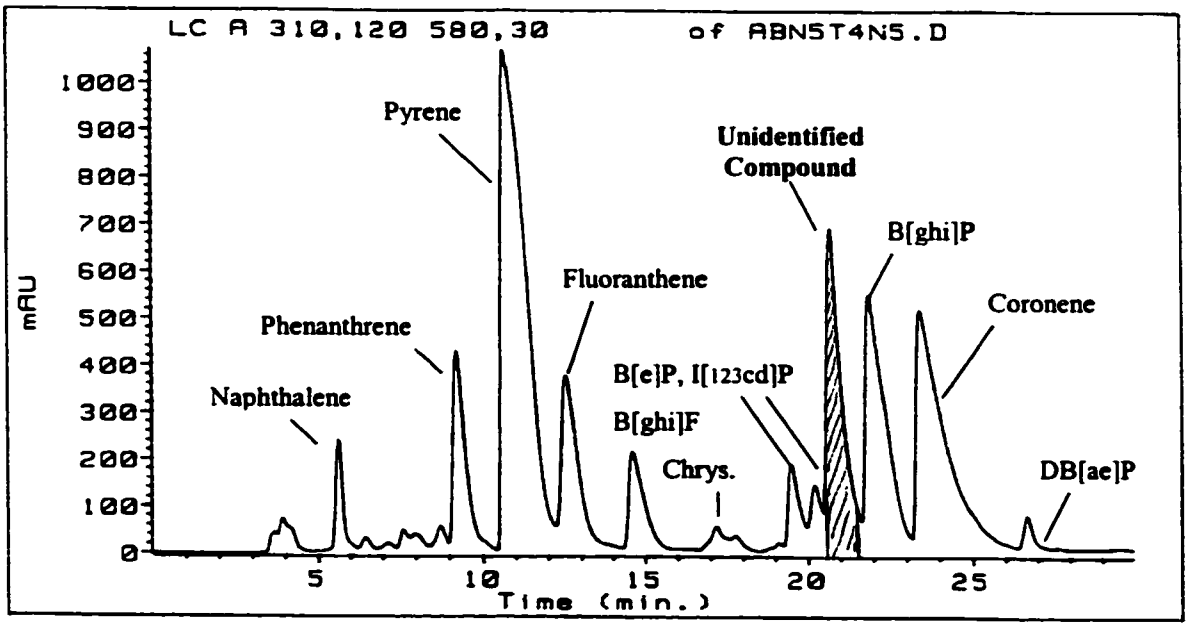
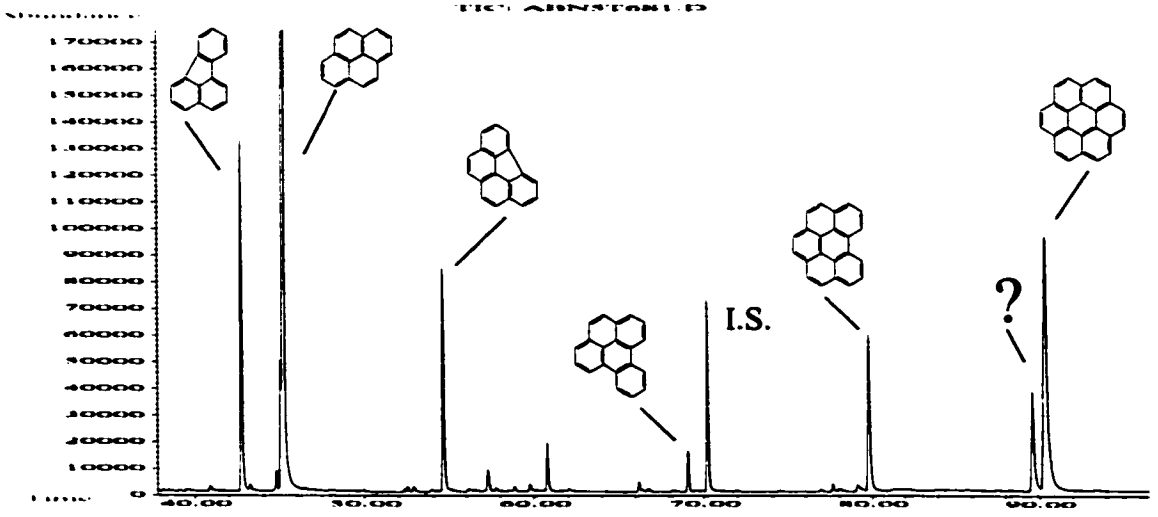


Figure 3-1: Normal phase HPLC chromatogram showing the unidentified compound in carbon black N550 extract (injection of an equivalent of approximately 400 mg of extracted carbon black sample in 20 uL of solution). Abbreviations: B[ghi]F=benzo[ghi]fluoranthene, Chrys.=chrysene (coeluting with cyclopent[cd]pyrene), B[e]P=benzo[e]pyrene, I[123cd]P=indeno[1,2,3-cd]pyrene, B[ghi]P=benzo[ghi]perylene, DB[ae]P=dibenzo[a,e]pyrene (analysis conditions in Appendix III).

Figure 3.2: GC-MS total ion chromatogram of a toluene extract of carbon black N550. (I.S. = internal standard, d_{12}-perylene)



3.3. IDENTIFICATION OF THIACORONENE IN CARBON BLACK EXTRACT

While many studies have succeeded in extracting and identifying PAC of molecular mass 300 and lower from carbon black, many compounds with higher molecular masses (300 to 448 Da) have been observed but remain unidentified. Tentative structural assignments have been made for some of these large and highly-condensed aromatic compounds.[100] In the present experiment, carbon black N550 was Soxhlet extracted with toluene and analyzed using normal phase HPLC. The same unidentified peak seen in N330 extract was also observed, eluting near benzo[ghi]perylene and coronene.

3.3.1. Isolation and Identification of Thiacoronene in Carbon Black

In an effort to provide enough extracted material from carbon black to allow the isolation and identification of unknown compounds, a series of carbon black extracts were prepared. Large-scale extractions of carbon black N550 were performed using toluene. A total of four 24-hour Soxhlet extractions were carried out (total mass of carbon black: 36.17 g) and combined. This composite toluene extract was analysed by semi-preparative normal phase (HPLC - normal phase analysis conditions in Appendix III). The compound which could not be identified through matching with library UV spectra was collected (Figure 3.1) and analysed by GC-MS, fluorescence and UV-VIS spectroscopy and probe mass spectrometry at both low and high resolutions.

Mass Spectrometric Analysis:

The low-resolution mass spectrum showed a molecular ion at m/z 306 and a doubly-charged molecular ion at m/z 153. High resolution mass spectral analysis (Figure 3.3) yielded an accurate mass value of 306.0507 corresponding to a number of possible molecular formulae ($C_{22}H_{10}S$, $C_{25}H_6$, $C_{19}H_{14}S_2$, $C_{21}H_8NO_2$, $C_{17}H_{10}N_2O_2S$, $C_{16}H_8N_3O_4$, $C_{19}H_6N_4O$); the most probable formula was thought to be $C_{22}H_{10}S$. Consideration of possible molecular structures consistent with this formula led to the proposal of a structure similar to benzo[ghi]perylene with the addition of a 5-membered sulfur ring. A literature search for the chemical substance name in the ring indices of the Chemical Abstracts yielded benzo[6,7]perylo[1,12-bcd]thiophene as a candidate.

The accurate mass value from high resolution mass spectrometry (306.0507) was nearly identical to that reported by DuVernet *et al.* (306.0505) and Dopper *et al.* (306.051) for synthetic benzo[6,7]perylo[1,12-bcd]thiophene (thiacoronene).[142,143] DuVernet's synthetic thiacoronene was identified through NMR spectroscopy and HR-MS.

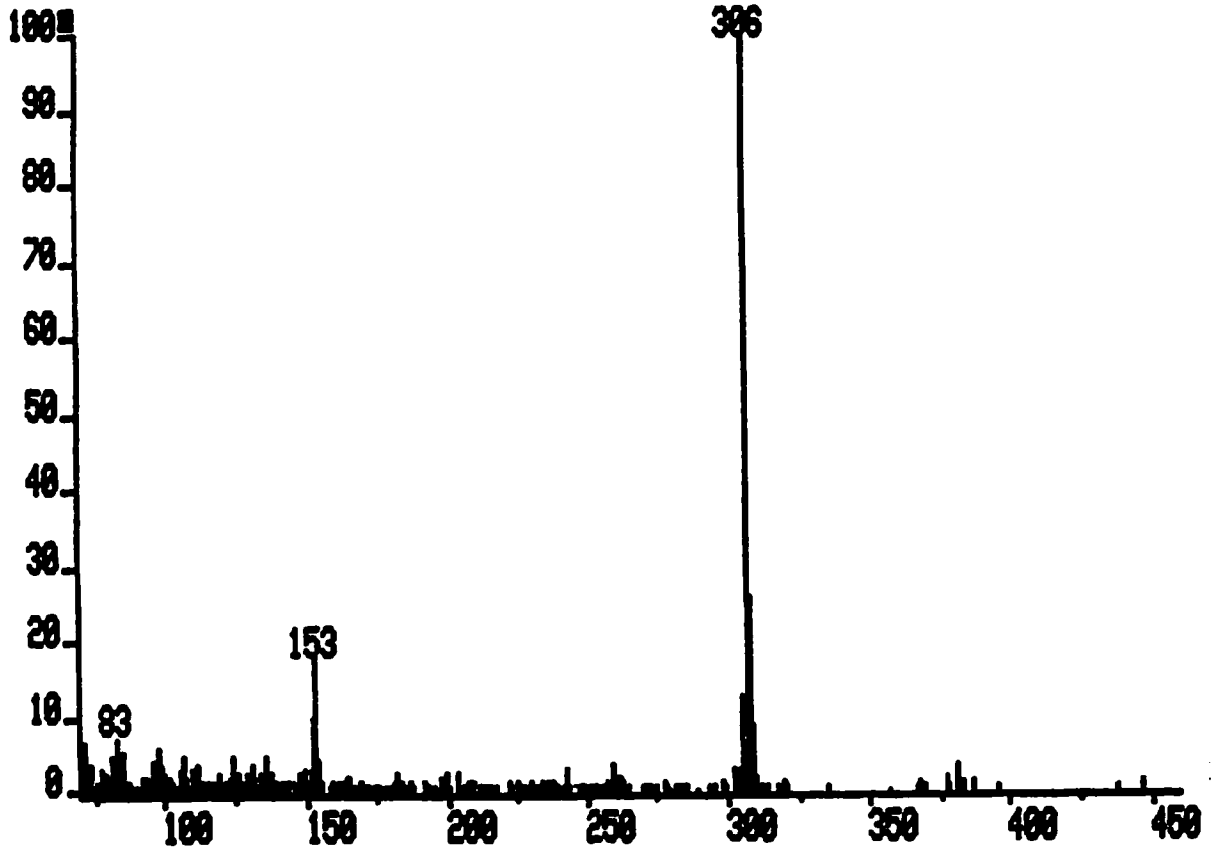


Figure 3.3: High resolution mass spectrum of the unidentified HPLC fraction.

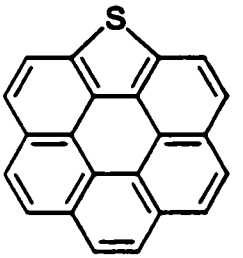


Figure 3.4: Structure of the proposed compound: Thiacoronene (benzo[6,7]perylo[1,12-bcd]thiophene).

The thiacoronene structure was proposed by Lee *et al.* for a late-eluting compound identified in their GC-MS studies of carbon black extracts;[102] however, this identification could not be confirmed due to the unavailability of a standard. The structure was proposed because it seemed reasonable when compared to structures of other PAH identified in the mixture.

In their reversed-phase HPLC studies of sulfur heterocyclic PAC, Colmsjo *et al.* reported that most sulfur-substituted PAH elute prior to their respective PAH analogues.[103] As benzo[ghi]perylene is the PAH analogue of thiacoronene, this prediction agrees with our observation that thiacoronene elutes just prior to B[ghi]P in our normal-phase HPLC study (see Figure 3.1). Through synthetic confirmations, Colmsjo also reported other sulfur-substituted PAH in the carbon black soot sublimate, such as sulfur-substituted B[a]P, B[e]P and triphenylene at relatively low levels as compared to thiacoronene, none of them quantified.[103]

UV spectrum:

The UV spectrum ($CHCl_3$) showed absorbance maxima at 307, 366 and 390 nm, values nearly identical to those reported by Dopper and Wynberg for synthetic thiacoronene (Figure 3.5).[143] The UV spectrum of thiacoronene is very similar to that of coronene; the alpha band of thiacoronene at 307 nm has a greater intensity and the beta band at 366 nm, a lesser intensity than coronene.

X-ray crystallographic analysis:

A sample of thiacoronene which had been isolated by preparative HPLC analysis evaporated to dryness slowly in a vial placed in a refrigerator, yielding three small light yellow-green crystals approximately 3 mm in length. Each one of these crystals was subjected to single crystal X-ray analysis. An X-ray diffraction data set was obtained by Dr. J. Britten and the structure was solved by Dr. R. Ruffolo (Figure 3.6). The R-factor for this structure was about 20% which was probably due to the presence of differently-ordered structures within the same crystal. This disorder would make it difficult to resolve and refine the individual structures that were present in the crystal. The data, however, were of sufficient quality to confirm the connectivity and structure of the molecule. The X-ray data confirmed that the structure of thiacoronene was planar.

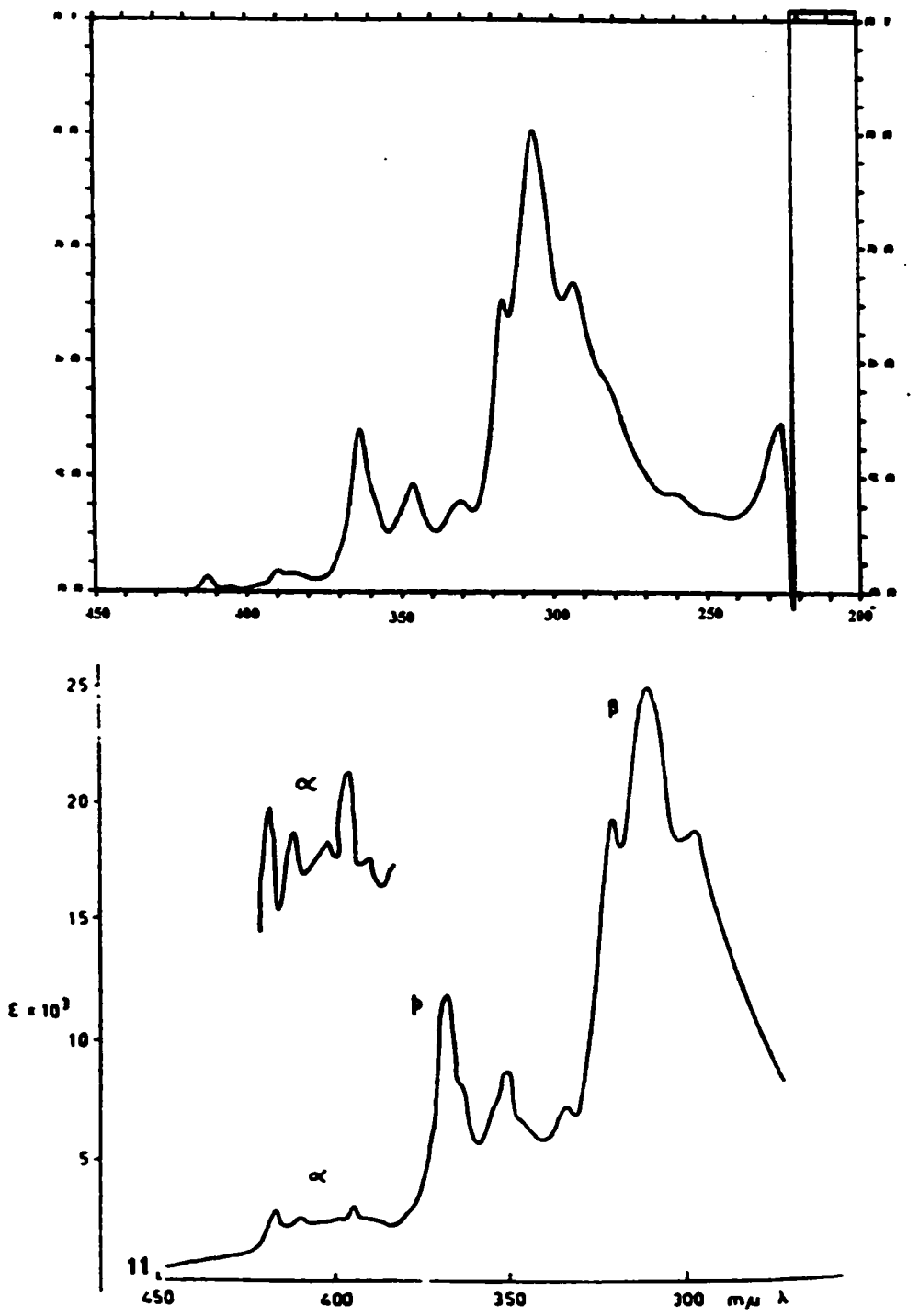


Figure 3.5: Bottom: UV-Vis spectrum of synthetic thiacoronene[117], top: UV-Vis spectrum of the unidentified HPLC fraction from carbon black extract.

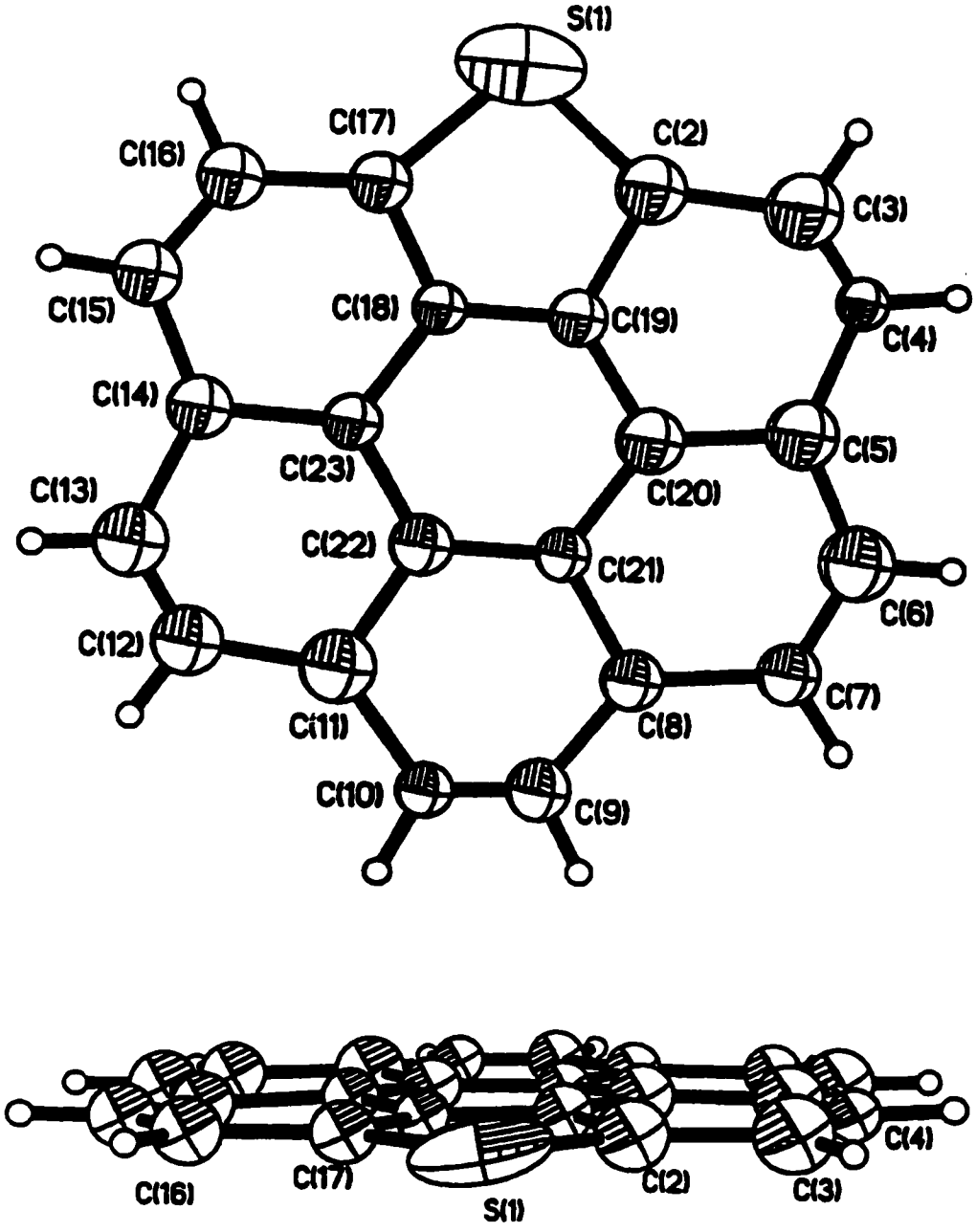


Figure 3.6: X-ray crystal structure of thiacoronene.

3.4. ANALYSIS OF CARBON BLACK PRODUCTS

Thiacoronene is classified as a thia-arene, a polycyclic aromatic compound which contains sulfur. Thia-arenes are found in sulfur-containing fuels, and are released into the atmosphere by combustion. These sulfur heterocycles have been found to be useful as source tracers because they are produced by fewer sources than PAH and are less ubiquitous in the environment.[144,145] In order to use thiacoronene as a source tracer, we needed to determine the levels of thiacoronene in different types of carbon blacks.

3.4.1. PAC in 12 Carbon Blacks

Columbian Chemicals Canada Ltd. produces a number of different carbon blacks in Hamilton, each tailored to a specific end-use. A total of 12 different carbon black products were made available to us for this study. These samples encompassed the majority of carbon black products made at Columbian's Hamilton plant as well as carbon black products manufactured worldwide. It was anticipated that individual carbon blacks that had been prepared under different production conditions and from different feedstocks would have similar PAC profiles, but would have different PAC levels and thiacoronene contents. Each carbon black (approximately 2 g) was extracted for 24 hours with toluene and the resulting extract was analysed by normal phase high performance liquid chromatography (HPLC) and by GC-MS; the PAC levels determined by GC-MS in the 12 carbon blacks are listed in Appendix V. The PAC in these extracts were identified using the retention times and UV spectra of PAH standards in HPLC analyses; in GC-MS

analyses, the retention time and mass spectral data were used. GC-MS chromatograms of three carbon blacks with compound identifications are shown in Figure 3.7.

Analyses of these carbon blacks illustrated the large differences in the levels of compounds adsorbed to different types of carbon blacks. Carbon black C1150, one of the purest carbon black products, is manufactured in small quantities from a coal tar distillate, while carbon blacks N330, N550 and R820 are standard grades of carbon black which are produced in mass quantities for rubber manufacture. The extracts from the "C" series carbon blacks like C1150 showed extremely low PAC levels. The other carbon blacks had PAC profiles similar to that seen for carbon blacks N550 and R820.

3.4.2. Thiacoronene in 12 Carbon Blacks

The thiacoronene contents of 12 carbon blacks were determined by GC-MS analysis. These values ranged from 0.002 to 43.2 μg/g with two carbon blacks as non-detects (<0.0003 μg/g) (see Table 3.2). Carbon blacks in the "N" and "R" series were found to have thiacoronene levels between 2.2 - 43.2 μg thiacoronene per gram of carbon black while carbon blacks in the "C" series contained low levels of thiacoronene (less than 0.01 μg/g). Emissions of carbon black from the plant will probably reflect the mix of carbon blacks produced on a given day. Thus, the thiacoronene levels in carbon black emissions from the plant may be represented by a weighted average of thiacoronene levels in the carbon blacks produced on a given day.

Figure 3.7: GC-MS total ion chromatograms of toluene extracts of three different carbon blacks (top – N234, middle – N330, bottom – C7011). Peak numbers correspond to those in Table 4.8 (I.S.=internal standard, d_{12}-perylene).

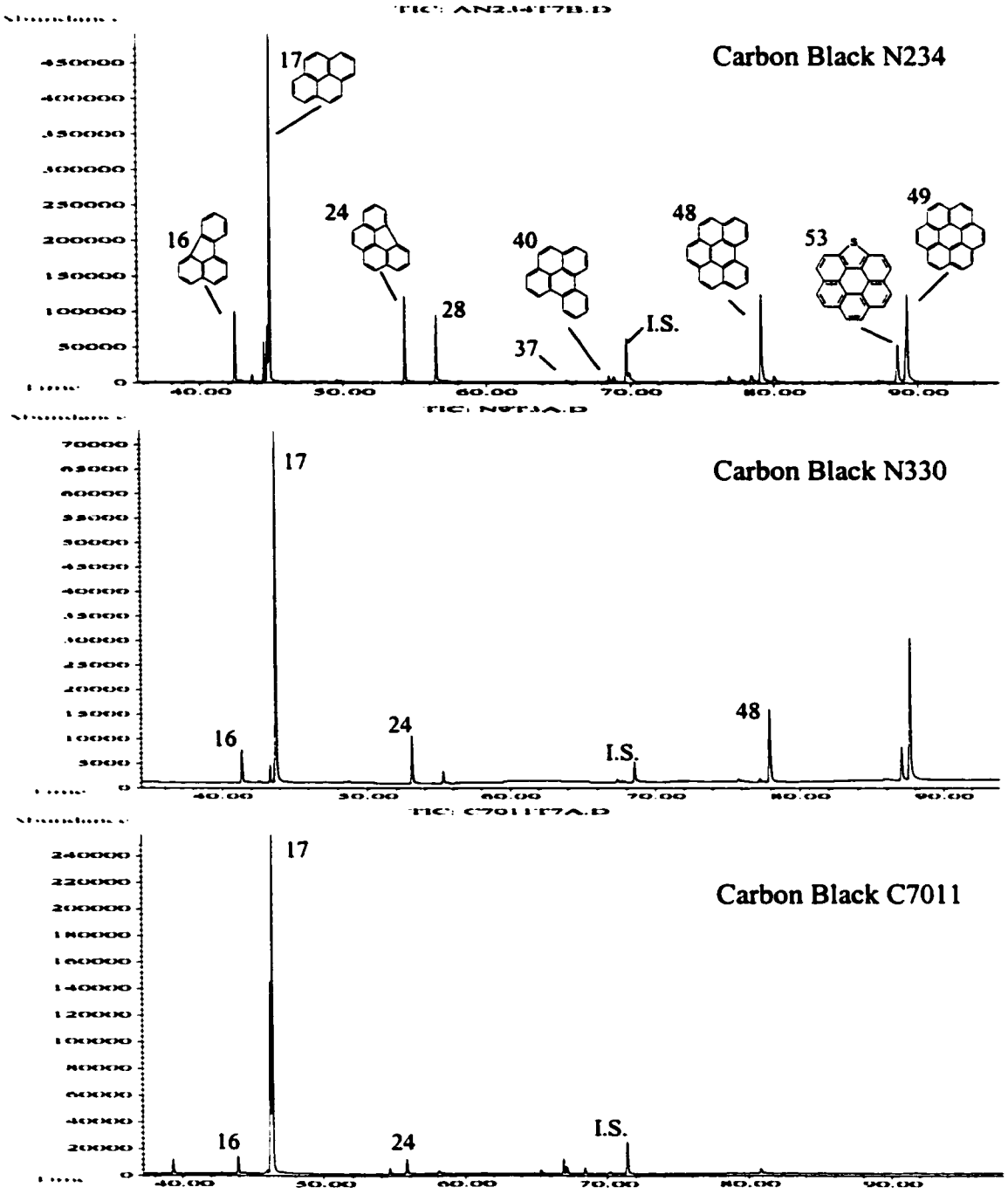


Table 3.2: Concentrations of thiacoronene in 12 carbon blacks produced by Columbian Chemicals Canada Ltd.

Carbon Black	Concentration of Thiacoronene (μg/g)
R820	43.5
N234	40.1
N330	17.8
N299	17.5
N660	14.9
N220	10.8
N650	9.2
N550	4.4
N326	2.2
C7011	0.0043
C1489	0.0052
C1150	<0.0003

Lee *et al.* found that the relative amounts of PAH associated with carbon blacks were quite dependent on the conditions of carbon black formation (e.g., furnace temperature and the nature of the feedstock).[102] They concluded that the absence of sulfur compounds in carbon blacks produced from natural gas, as compared to feedstocks containing sulfur indicated that organic sulfur persists in the combustion of sulfur-containing petroleum feedstocks and appears as sulfur-containing polycyclic compounds associated with carbon black. This conclusion is consistent with our observations. Carbon blacks in the "C" series were determined to have low or non-detectable levels of thiacoronene, as these carbon blacks originate from a low-sulfur feedstock. The low thiacoronene levels in "C" series carbon blacks do not present a problem for our method.

"C" series carbon blacks are not widely produced. The ranges of "N" and "R" carbon blacks represent the majority of the production volume at the carbon black plant.

3.5. DEVELOPMENT OF A SEQUENTIAL EXTRACTION METHOD

There are a number of potential problems that may be associated with the detection of carbon black in ambient air. The large variety of particulate sources in urban atmospheres poses difficulties in any source apportionment effort. The levels of carbon black found in air particulate in Hamilton were anticipated to be extremely low compared to those of other particulate sources such as soils, road dusts, vehicular particulates, coal and coking emissions. Each of these particulate sources provides its own contribution to the overall chemical profile of compounds adsorbed to particles in the atmosphere. The background of chemicals associated with air particulate includes trace metals, minerals, and organics such as biologically-degraded organic matter, hydrocarbons, and other compounds derived from anthropogenic sources.

The majority of organic compounds in air particulate are easily extractable. Carbon black, on the other hand, has surfaces to which organic chemicals are very strongly adsorbed. Polycyclic aromatic compounds are strongly adsorbed to the planar aromatic substructures of carbon black. Stenberg *et al.* stated that a dominant factor that will influence the extraction of a PAC from carbon black is its π-electron system, and that the strength of the interaction between the matrix and the component to be extracted is dependent on aromaticity.[138] Published experiments compared the relative extraction efficiencies of benzene, toluene and cyclohexane;[140] methanol, dichloromethane,

cyclohexane and acetone;[138] and benzene and naphthalene [137] for carbon black extraction. The experiments showed that: (i) of the non-aromatic solvents, dichloromethane had the best extraction ability, and (ii) aromatic solvents such as toluene and naphthalene were superior in their extraction yields as compared to non-aromatic solvents like cyclohexane.

We proposed that a sequential extraction approach may be useful as part of a method to detect carbon black in ambient air. Twenty-four hour dichloromethane extractions are commonly used to extract organic compounds from air particulate material and other matrices and are generally viewed as achieving complete extraction.[27,50] Our goal was to find an aromatic solvent that could be used after extraction with dichloromethane to extract strongly adsorbed PAC from carbon black. In the literature, no direct comparisons had been made between dichloromethane and aromatic solvents such as toluene or chlorobenzene. In the present research, these solvents, dichloromethane, toluene and chlorobenzene were evaluated for their relative extraction efficiencies in the extraction of PAC from carbon black.

3.5.1. The Preliminary Evaluation of Carbon Black Extraction with Various Solvents

Preliminary experiments were carried out in order to compare the extraction efficiencies of dichloromethane and toluene in the extraction of carbon black. Carbon black type N550 (a rubber-grade carbon black used in the carcasses of tires and produced from decanted oil from refinery bottoms), was chosen for our preliminary extraction study as it represents a typical carbon black and a major portion of the production at Columbian. In these experiments, two equal portions (9.0 g each) of carbon black N550

were extracted for 24-hours in a Soxhlet apparatus in parallel as shown in Figure 3.8. The first portion underwent a sequential extraction, first with dichloromethane (termed by the author as an initial dichloromethane extraction) and subsequently with toluene (termed as a subsequent toluene extraction). The second portion of carbon black underwent a toluene extraction only. It was expected that in a sequential extraction, any PAC that remained adsorbed to carbon black following extraction with dichloromethane would be extracted by toluene in the subsequent extraction. The combination of these sequential extracts would then be expected to afford a total level of PAC similar to that achieved by a single toluene extraction. It was also expected that toluene would show a higher extraction efficiency for high molecular weight PAC than would dichloromethane.

GC-MS analyses were performed on each extract and results were compared for various PAC (see Figure 3.9). High molecular weight PAC (such as benzo[ghi]perylene - peak 48, coronene - peak 49, and thiacoronene - peak 53) were obtained in substantially higher levels in both initial and subsequent toluene extracts than in the dichloromethane extract (15 to 30 times higher). Overall, we observed that the sequential extraction methodology resulted in the extraction of compounds that are weakly adsorbed to carbon black (low-mass PAC) during the dichloromethane extraction, and the extraction of more strongly adsorbed, high molecular mass compounds during subsequent extraction with toluene.

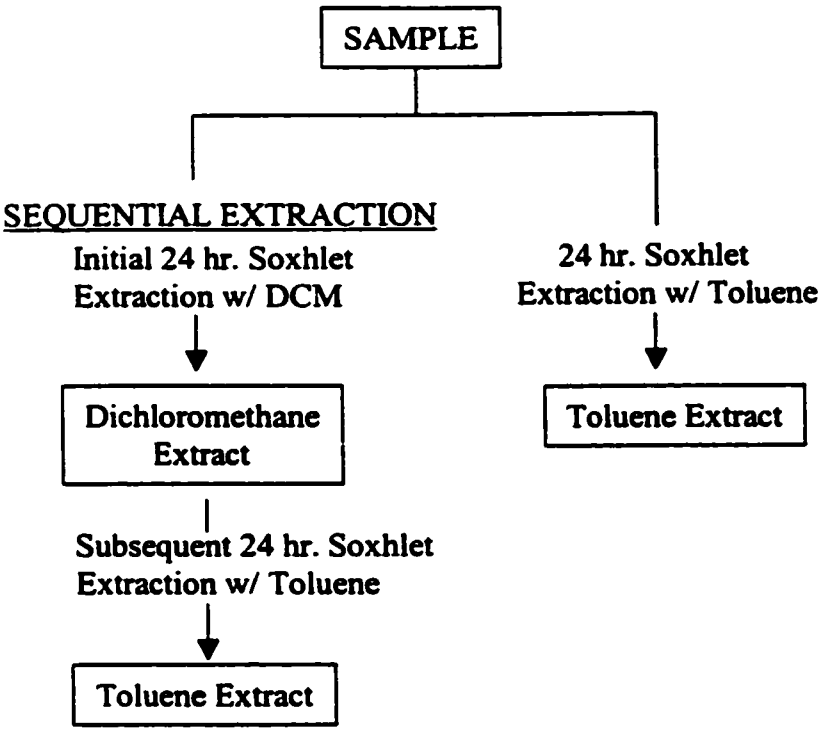
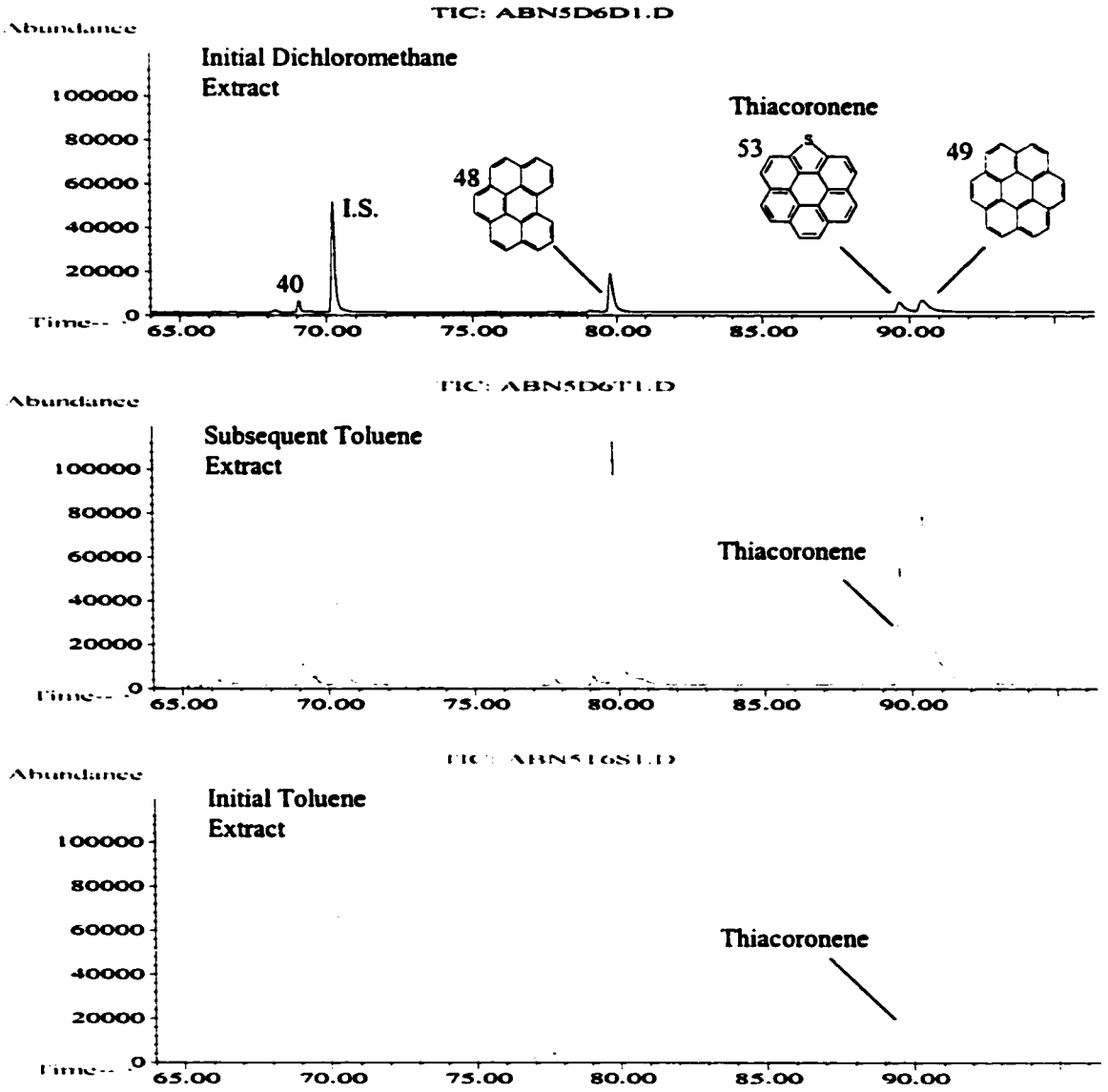


Figure 3.8: Flow diagram of sequential extraction versus toluene extraction for carbon black.

Figure 3.9: GC-MS total ion chromatograms of carbon black N550 extracts (top - initial dichloromethane extract, middle - subsequent toluene extract, bottom - initial toluene extract). Peak numbers correspond to those in Table 4.8 (I.S.= internal standard, d_{12}-perylene).



3.5.2. Evaluation of Extraction Efficiencies and Reproducibilities

Our preliminary findings showed that a strong aromatic solvent was required to provide more forceful extraction of strongly adsorbed PAC from carbon black. A comparative study of the extraction efficiencies of dichloromethane, toluene and chlorobenzene for carbon black was undertaken. Each of these solvents was evaluated as an extracting solvent for carbon black on its own. In addition, toluene and chlorobenzene were evaluated as subsequent extracting solvents following an extraction with dichloromethane. Three replicates for each experimental trial (six replicates for dichloromethane) were performed giving a total of 24 sample extracts. All PAC were quantified, providing average PAC levels and standard deviations and extraction reproducibility data.

In Figure 3.10, the sequential extractions using dichloromethane as the initial solvent and (a) toluene, and (b) chlorobenzene as the subsequent extracting solvents are shown. Low molecular weight PAC are mainly extracted by dichloromethane (shown as light grey bars) in the sequential extraction, while the majority of high molecular weight PAC are extracted by toluene and chlorobenzene (black bars). Figure 3.11 compares toluene and chlorobenzene as initial extracting solvents. The relative amounts of PAC extracted by these two aromatic solvents are very close, and in most cases, within one standard deviation of each other.

Toluene and chlorobenzene, as initial solvents had higher extraction efficiencies (approximately 50% higher) in the extraction of low-to-moderate molecular mass PAC (like fluoranthene, pyrene and benzo[ghi]fluoranthene) than dichloromethane. While the concentration of fluoranthene averaged 8.8 μg/g in the dichloromethane extractions, toluene and chlorobenzene yielded 14-15 μg/g (see Table 3.4). Similarly, for pyrene, the average concentrations in toluene and chlorobenzene were almost double those found in dichloromethane (150, 150 and 96 μg/g respectively - see Table 3.4). In addition, higher molecular mass compounds (especially benzo[ghi]perylene, coronene and thiacoronene) were obtained in substantially higher levels in both initial and subsequent extracts using toluene and chlorobenzene than in dichloromethane extracts (5 to 32 times higher - see Figure 3.10 and Figure 3.11). Average concentrations of benzo[ghi]perylene varied from 31 to 41 μg/g in toluene and chlorobenzene, and averaged 6.4 μg/g in dichloromethane (Table 3.4). Thiacoronene concentrations in toluene and chlorobenzene averaged 17-19 μg/g and only 1.3 μg/g in dichloromethane (see Table 3.3). These relative extraction efficiencies are also expressed in terms of percentages for the two sequential extractions in Table 3.5.

Overall, PAC with molecular weights ranging from 202 Da (fluoranthene) to 226 Da (cyclopenta[cd]pyrene) were efficiently extracted (80 - 90%) using dichloromethane (see Table 3.5). In contrast, 83 - 97% of PAC with molecular weights above 252 Da (indeno[1,2,3-cd]pyrene to coronene) were found in the subsequent toluene and chlorobenzene extracts. The fraction of the total thiacoronene extracted from carbon

black in the initial dichloromethane extraction was less than 8%, while the subsequent toluene or chlorobenzene extractions removed the remainder of the thiacoronene from carbon black (93 ± 1.6 % of the thiacoronene for toluene and 93 ± 2.0% for chlorobenzene).

Toluene was determined to be the most practical choice for the subsequent extraction solvent. The levels of thiacoronene detected in the subsequent toluene and chlorobenzene extracts were not significantly different. The lower boiling point of toluene leads to greater ease of sample handling (including vacuum- and nitrogen-assisted evaporation and chromatographic steps). Also, the availability of high quality toluene and the comparatively lower health hazards made toluene the best choice.

Table 3.3: Summary of extraction efficiency data for thiacoronene in carbon black N330.

Extracting Solvent	Average Thiacoronene Level (μg/g)	Standard Deviation	RSD (%)
Initial Dichloromethane Extraction (n = 6)	1.33	0.25	19
Initial Toluene Extraction (n = 3)	17.8	0.75	4.2
Initial Chlorobenzene Extraction (n = 3)	19.2	1.01	5.2
Subsequent Toluene Extraction (n = 3)	17.3	0.28	1.6
Subsequent Chlorobenzene Extraction (n = 3)	17.8	0.36	2.0

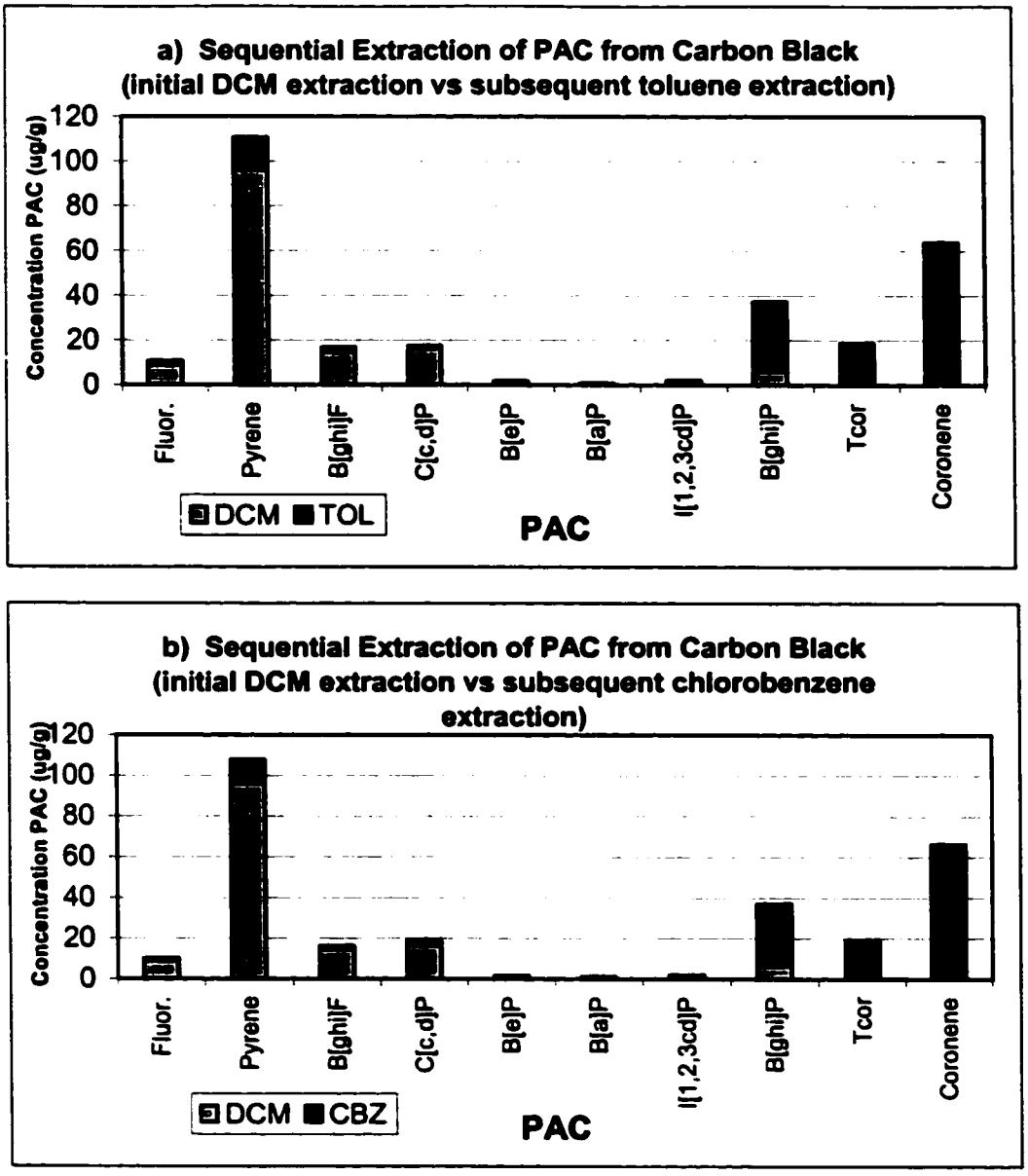


Figure 3.10: Relative amounts of PAC extracted in sequential extractions of carbon black N330 using dichloromethane as the initial extracting solvent and (a) toluene, and (b) chlorobenzene as the subsequent extracting solvents.

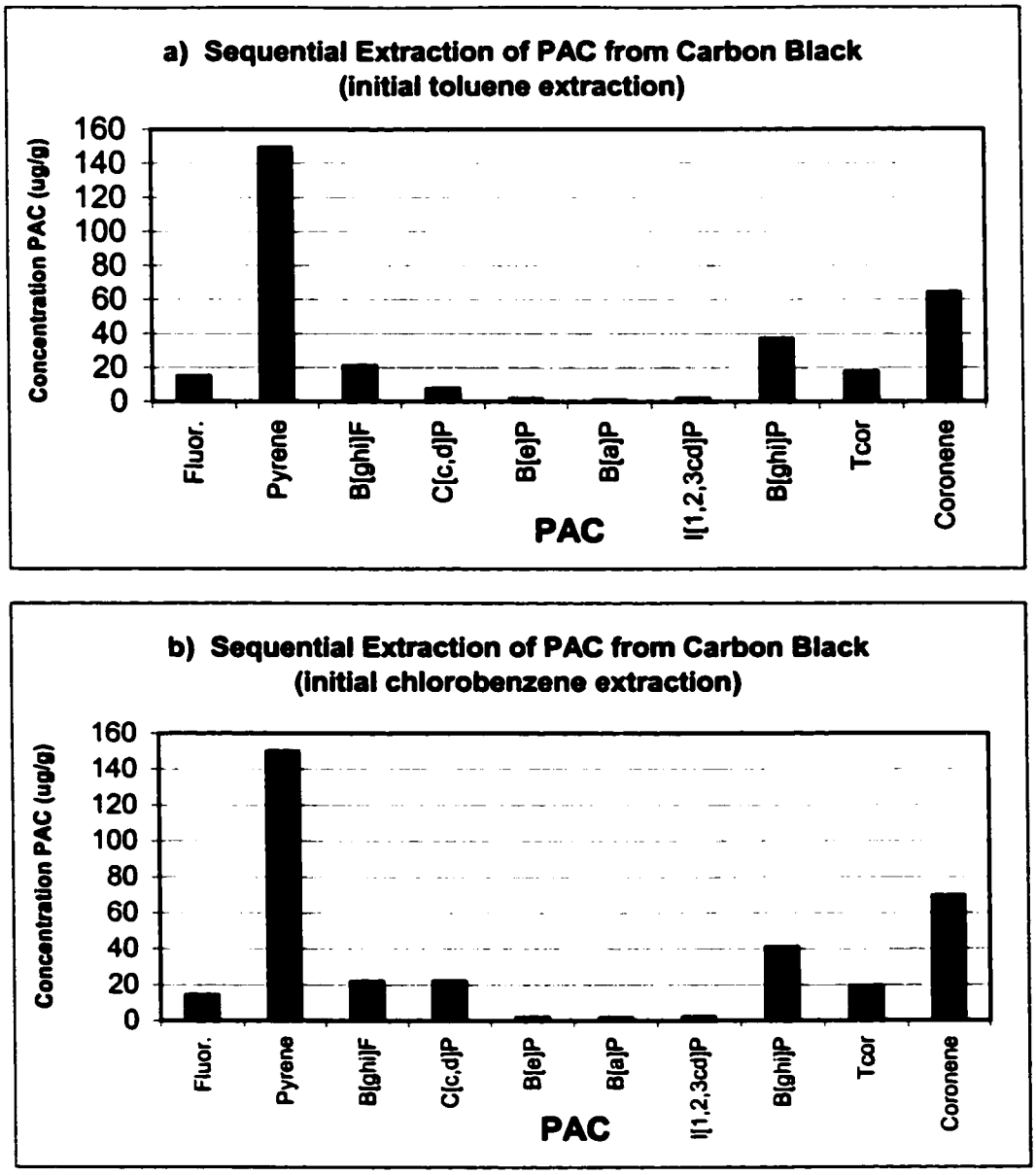


Figure 3.11: Relative amounts of PAC extracted in initial extractions of carbon black N330 using (a) toluene and (b) chlorobenzene as the initial extracting solvents.

Table 3.4: Amounts of PAC extracted in single and sequential Soxhlet extractions of carbon black N330 using dichloromethane as the initial extraction solvent and toluene and chlorobenzene as both initial and subsequent extracting solvents.

Polycyclic Aromatic Compound	Initial DCM Extract (ug/g; n=6) Average (SD)	Initial Toluene Extract (ug/g; n=3) Average (SD)	Initial CBZ Extract (ug/g; n=3) Average (SD)	Subsequent Toluene Extract (ug/g; n=3) Average (SD)	Subsequent CBZ Extract (ug/g; n=3) Average (SD)
Fluoranthene	8.8 (0.57)	15 (0.90)	14 (0.43)	2.0 (0.13)	1.4 (0.39)
Pyrene	96 (2.3)	150 (8.8)	150 (5.4)	15 (0.46)	12 (2.6)
Benzo[ghi]fluoranthene	15 (0.86)	21 (1.2)	22 (0.46)	2.2 (0.08)	1.7 (0.16)
Cyclopenta[cd]pyrene	16 (1.2)	7.7 (2.1)	22 (0.54)	1.2 (0.76)	2.7 (0.40)
Benzo[e]pyrene	1.1 (0.09)	1.7 (0.11)	1.9 (0.04)	0.64 (0.02)	0.48 (0.09)
Benzo[a]pyrene	0.20 (0.03)	0.93 (0.32)	1.7 (0.04)	0.68 (0.35)	1.1 (0.22)
Indeno[1,2,3-cd]pyrene	0.17 (0.03)	2.1 (0.20)	2.1 (0.14)	1.9 (0.20)	1.8 (0.31)
Benzo[ghi]perylene	6.4 (1.01)	37 (2.8)	41 (1.4)	31 (1.7)	31 (1.4)
Thiacoronene	1.3 (0.25)	18 (0.75)	19 (1.0)	17 (0.28)	18 (0.36)
Coronene	2.2 (0.38)	64 (2.1)	69 (4.1)	62 (2.9)	64 (3.0)

Table 3.5: Percentages of PAC extracted in sequential Soxhlet extractions of carbon black N330 using dichloromethane as the initial extraction solvent and toluene and chlorobenzene as subsequent extracting solvents.

Polycyclic Aromatic Compound	Initial DCM Extract (average; n=6) (ug/g)	Subsequent Toluene Extract (average; n=3) (ug/g)	Initial DCM Extract (average; n=6) (ug/g)	Subsequent CBZ Extract (average; n=3) (ug/g)
Fluoranthene	81.4	18.6	86.5	13.5
Pyrene	86.7	13.3	89.1	10.9
Benzo[ghi]fluoranthene	86.9	13.1	89.6	10.4
Cyclopenta[cd]pyrene	93.3	6.7	85.6	14.4
Benzo[e]pyrene	63.7	36.3	70.2	29.8
Benzo[a]pyrene	22.8	77.2	16.0	84.0
Indeno[1,2,3-cd]pyrene	8.1	91.9	8.5	91.5
Benzo[ghi]perylene	17.0	83.0	17.1	82.9
Thiacoronene	7.1	92.9	7.0	93.0
Coronene	3.5	96.5	3.4	96.6

3.5.2.1. Reproducibility of Extractions and Instrumental Analyses

Variability amongst extraction replicates was greater for initial extractions versus subsequent extractions (initial extraction RSDs ranged from 4.2 – 15% while subsequent extractions RSDs ranged from 1.3 to 1.7%). The highest RSD was associated with the dichloromethane extraction. Instrumental reproducibility was assessed by analysing two sample extracts (initial toluene extract, trial 3 and initial chlorobenzene extract, trial 2) four times each in alternating injections. Instrumental reproducibility for the responses of all PAC quantified was assessed. For most PAC, the RSD for instrumental response ranged from 1.5 to 5.2%, while for PAC at or near detection limit, the RSD ranged from 6.1 to 12%.

3.5.3. Sequential Extraction of Ambient Air Particulate

An experiment was undertaken to evaluate the relative amounts of PAC extracted by dichloromethane and subsequently by toluene from urban air particulate. An ambient air sample collected in 1991 at a sampling site in the west end of Hamilton (MOE Station 29118) was expected to have low industrial impingements given the distance from the industrial sites and the prevailing wind direction. The filter was subjected to sequential extraction (dichloromethane then toluene) followed by cleanup and analysis via GC/MS. Results showed that the secondary toluene extract had very low levels of PAH compared to the dichloromethane extract. Levels of individual PAC were between 40-fold (thiacoronene) and 30,000-fold (pyrene) lower in the toluene extract as compared to the

levels detected in the initial dichloromethane extract.

Figure 3.12 (a) shows the levels of PAC from a sequential extraction of a typical Hamilton air particulate sample with no industrial impingements. Figure 3.12 (b) is a similar graph, but for an air particulate sample collected downwind of the steel industries in Hamilton. Note in both graphs that dichloromethane readily extracts compounds across the entire mass range. The subsequent toluene extracts in both the upwind and downwind samples appear constant in PAC profile and content. The principal difference is seen in the dichloromethane extracts, where the downwind sample contains significantly higher levels of PAC relative to the upwind sample. This illustrates the variability of PAC levels found upwind and downwind of Hamilton industry. Overall, the dichloromethane extraction of air particulate is quite efficient, leaving very little PAC behind for the toluene extraction.

The amounts of thiacoronene in the dichloromethane and toluene extracts of air particulate were determined using GC-MS (operated in selected ion monitoring mode). Thiacoronene was found at low-to-negligible levels in toluene extracts of these ambient air samples. In contrast, we have found that the levels of thiacoronene in the toluene extracts of carbon black are very high, supporting the use of thiacoronene as a source tracer for ambient carbon black. Overall, we have found that the relative levels of PAC in the sequential extracts of ambient air differ quite remarkably from those found in the sequential extracts of carbon black. While dichloromethane efficiently extracts low molecular weight PAC in both carbon black and air particulate, the high molecular weight PAC in carbon black require more forceful extraction conditions. In the sequential

extraction methodology, an initial dichloromethane extraction allows the removal of almost all of the organic compounds on air particulate but little of the high molecular weight compounds in carbon black. The subsequent toluene extraction removes the relatively small amount of organics remaining on air particulate, while removing a substantial amount of higher molecular mass PAC from carbon black. This fundamental difference in extractability of PAC from air versus carbon black led us to propose a method to identify ambient carbon black in air.

3.6. DETERMINATION OF CARBON BLACK IN AIR PARTICULATE

3.6.1. Differential Extraction of Thiacoronene and PAC in Air vs. Carbon Black

In the sequential extraction of Hamilton air samples, we have found that all air sampled upwind and downwind, near or far from the steel mills yield comparatively clean subsequent toluene extracts with relatively low total PAC levels. The analysis of the subsequent toluene extracts, whether upwind or downwind, show that nearly all of the PAC on air particulate is efficiently removed in the initial dichloromethane extraction, leaving negligible levels in the secondary toluene extract. In the sequential extraction of carbon black, approximately half of the PAC (the majority of which are high mass PAC) are found in the subsequent toluene extract. The chromatograms of carbon black extracts are much simpler, with fewer types of PAC and other compounds compared to air particulate extracts, the main difference being thiacoronene levels.

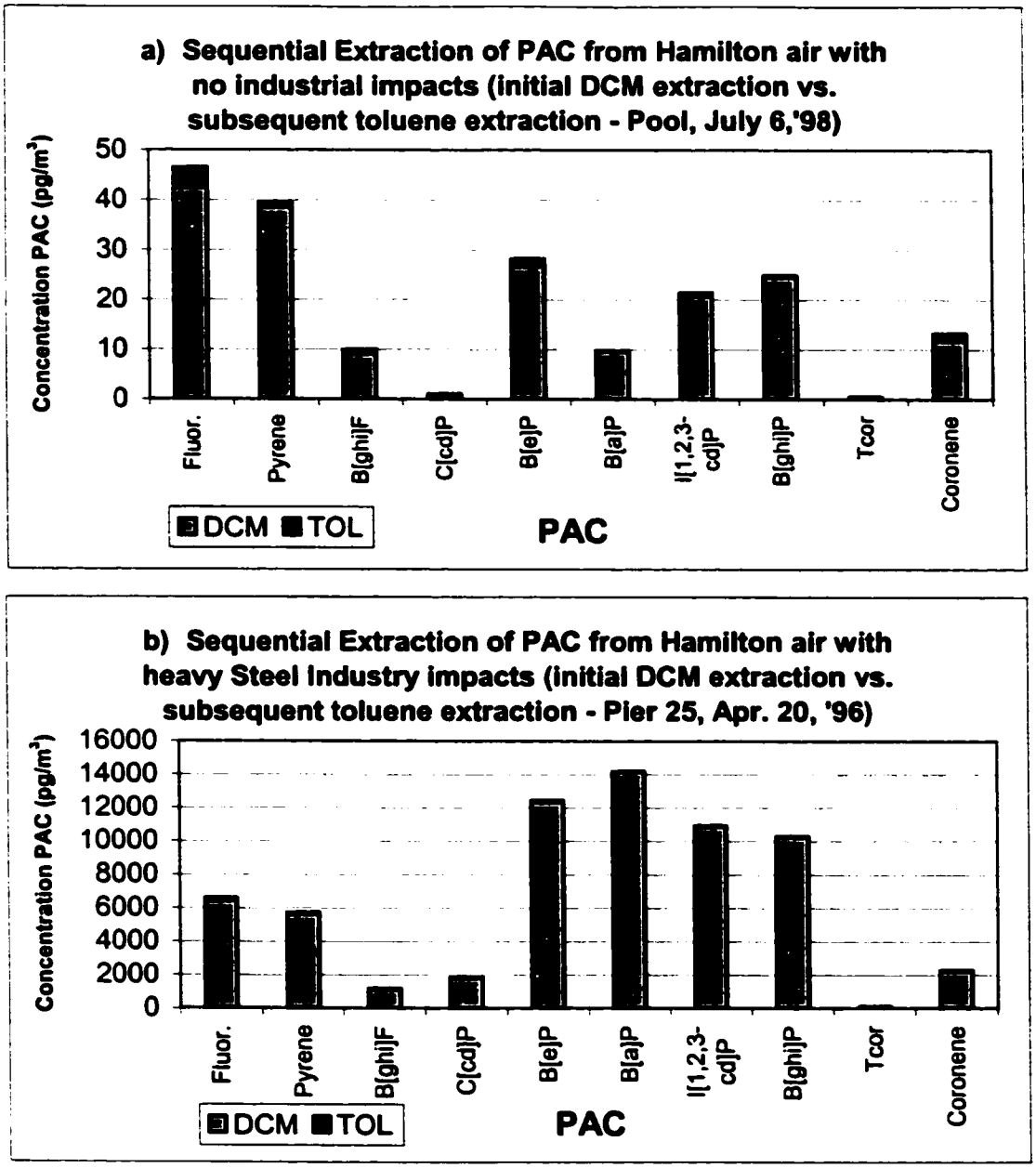


Figure 3.12: Relative amounts of PAC in Hamilton air in sequential extracts using dichloromethane as the initial extracting solvent and toluene as the subsequent extracting solvent for (a) background urban air with little industrial impact, and (b) urban air containing heavy steel industry impacts.

Figure 3.13: GC-MS total ion current chromatograms of the dichloromethane and toluene extracts of carbon black N330 and of ambient air sampled upwind of a carbon black plant: (a) dichloromethane extract of carbon black N330 (1mg equivalent of carbon black injected); (b) subsequent toluene extract of carbon black N330 (0.1 mg equivalent of carbon black injected); (c) dichloromethane extract of ambient air (40.5 m^3 equivalent of air injected); (d) subsequent toluene extract of ambient air (40.5 m^3 equivalent of air injected).

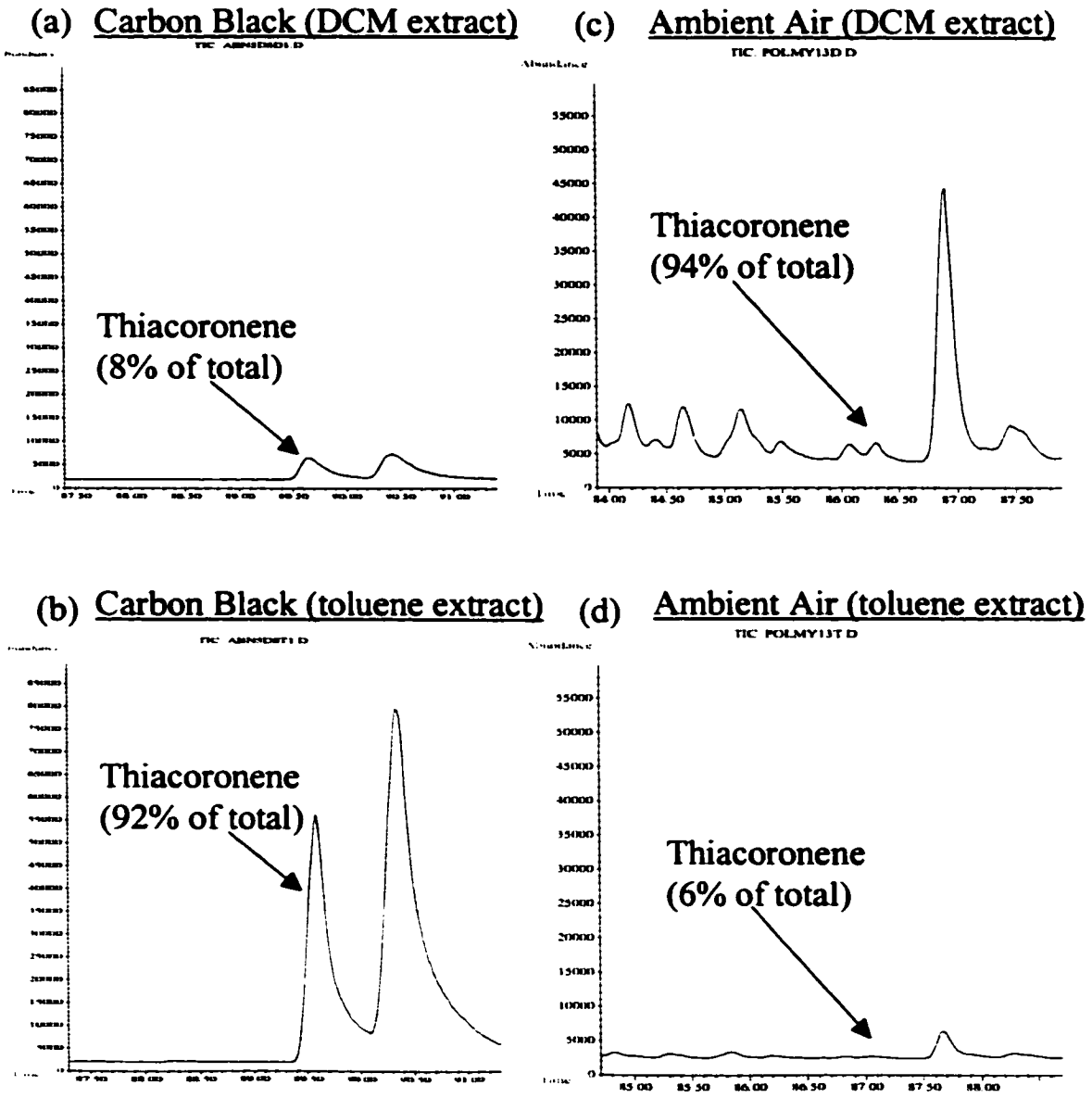


Figure 3.13 shows a comparison of thiacoronene levels in the GC-MS chromatograms of the dichloromethane and toluene extracts afforded by the sequential extraction of carbon black N330 and a sample of "background" air particulate collected upwind of the carbon black plant. The dichloromethane extract of air particulate contained almost all (94%) of the thiacoronene while the subsequent toluene extract contained the remainder (6%). The level of thiacoronene in the subsequent toluene extract of this air sample was very low (0.4 pg/m^3). The second extraction (using toluene) of the two-stage extraction procedure was found to be highly selective for the extraction of thiacoronene from carbon black (containing 92% of the thiacoronene); based on the corresponding extractions of ambient air particulate, it appeared that there would be little interference from background contributions due to air particulate.

Thiacoronene has been found at low-to-negligible levels in toluene extracts of ambient air samples, while the toluene extracts of carbon black contain relatively high levels of thiacoronene. These findings showed the promise of the use of thiacoronene as a source tracer for carbon black in air via analysis for thiacoronene in the toluene extracts of ambient air samples

3.6.2. Assessment of the Potential to Determine Carbon Black in Air Using Thiacoronene as a Source Tracer

3.6.2.1. Calibration of Analytes in Carbon Black Extract

Calibration curves for three high molecular mass PAC in carbon black extract were determined. Six concentrations of carbon black N550 extract ranging from 11.4 to 459

milligrams of carbon black extracted per sample (in 100 μL toluene) were prepared. The concentration ranges for benzo[ghi]perylene, coronene and thiacoronene and correlations for linear fit for each PAC calibrated were the following:

benzo[ghi]perylene:	0.01 - 4.6 ng injected; ($r^2 = 0.999$)
coronene:	0.03 - 12.7 ng injected; ($r^2 = 0.999$)
thiacoronene:	0.01 - 3.8 ng injected; ($r^2 = 0.999$)

The lowest concentrations injected were approximately 2 - 6 times the detection limit for these compounds (detection limit = 5 pg when S/N = 3). These calibration lines for the analysis of high mass PAC in carbon black extract showed that benzo[ghi]perylene, coronene and thiacoronene can be accurately quantified in carbon black extract over a concentration range of 3 orders of magnitude (see Figure 3.14).

3.6.2.2. Calibration Line for Thiacoronene

A calibration curve for the GC-MS analysis of thiacoronene isolated from carbon black (isolated during normal phase HPLC) was also produced. The calibration was performed using seven dilutions within the concentration range of 0.006 ng to 5.534 ng of thiacoronene injected (three replicates per dilution). The observed detection limit for thiacoronene was 2.5 pg injected (S/N = 3) and the correlation for linear fit was $r^2 = 0.999$ (see Figure 3.15). The detection limit for carbon black using thiacoronene as a source tracer is an injection equivalent of 0.17 μg of carbon black extracted (average concentration of thiacoronene in carbon black of 15 μg/g).

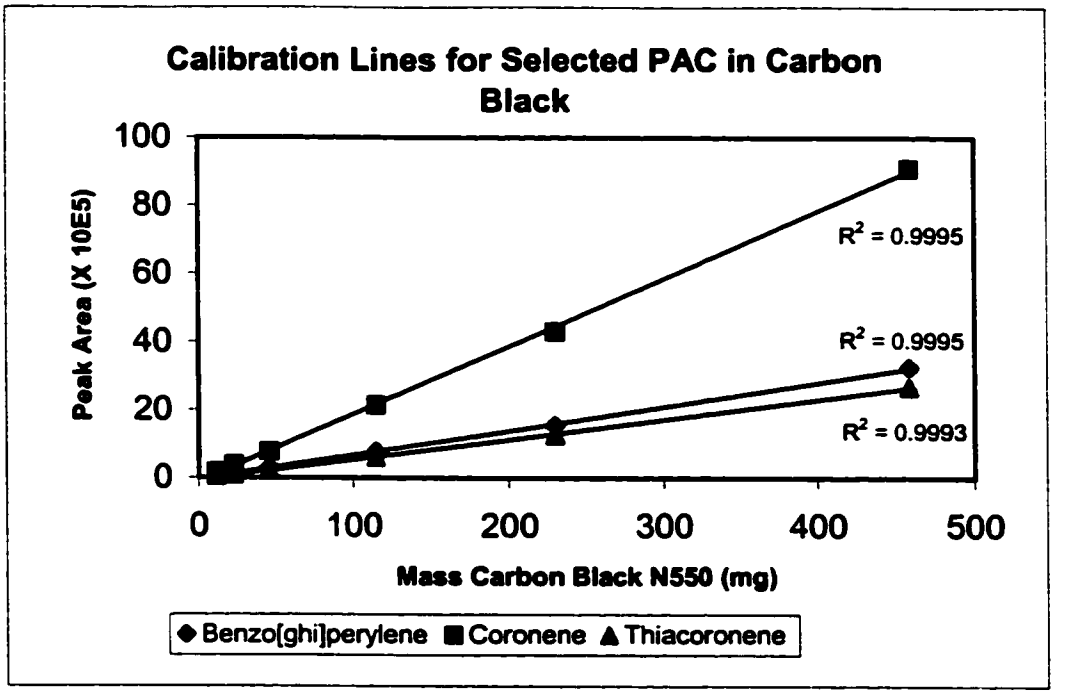
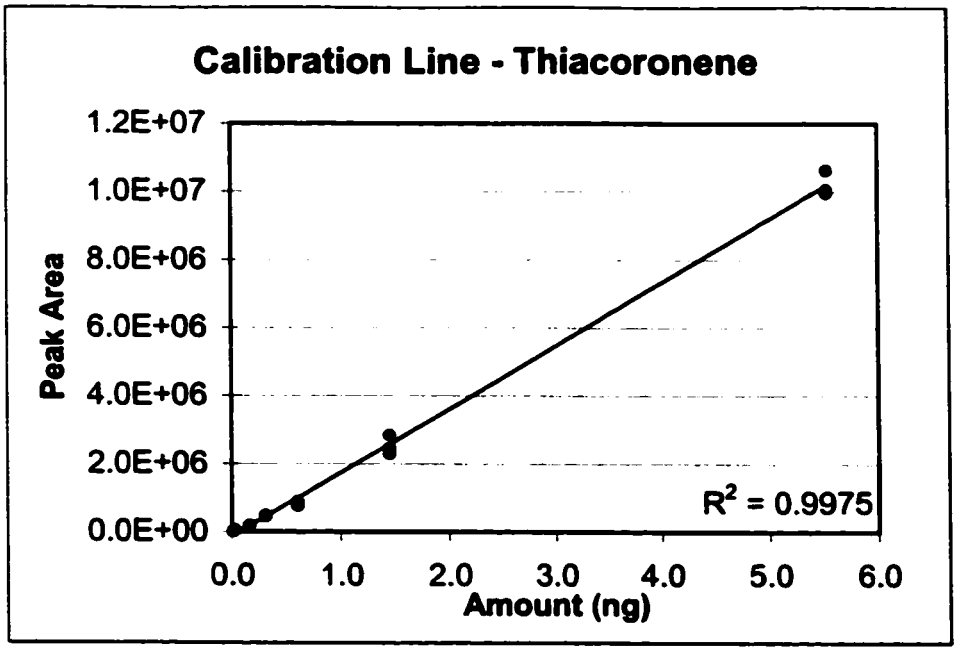


Figure 3.14: Calibration Lines for selected PAC in carbon black.



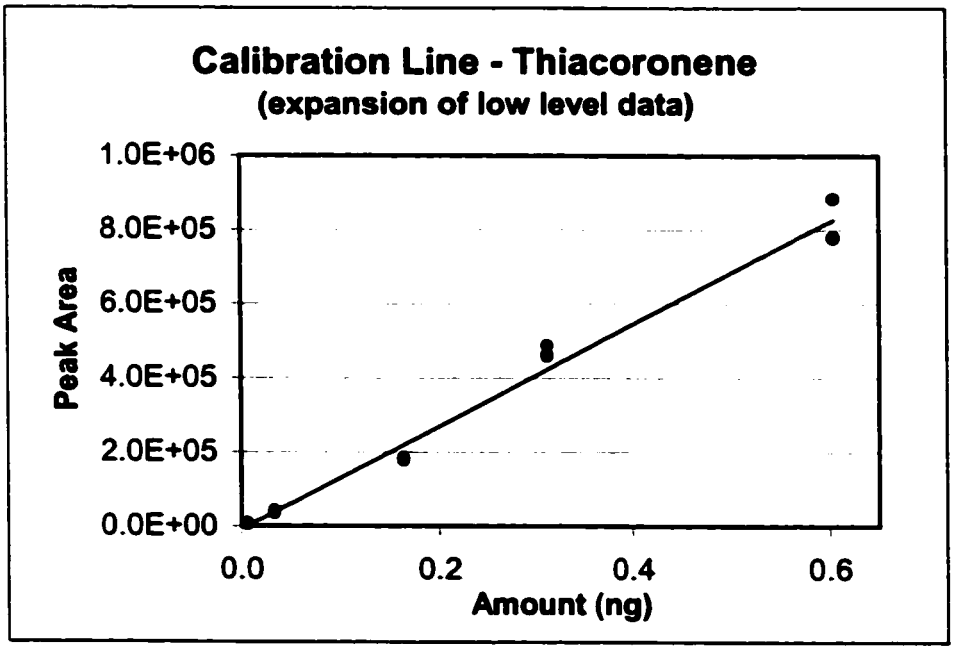


Figure 3.15: Calibration line for thiacoronene (thiacoronene standard series was prepared from thiacoronene isolated from a carbon black extract using normal phase HPLC). Bottom chart is an expansion of the low level region of the top chart.

3.6.2.3. The Carbon Black Spike Experiment

The purpose of this experiment was to evaluate whether we could determine the presence of small amounts of carbon black in the presence of air particulate material. Two separate air filter samples collected at the Main West site ((1) - filter # 00030, mass of particulate 0.03267 g, collected on 22/08/90, and (2) - filter #00028, mass of particulate 0.03121 g, collected on 20/08/90, both representing 1631 m^3 of air) were each divided into four equal parts. The filter portion masses were as follows: filter portion (1A) 0.543 g, (1B) 0.538 g, (1C) 0.541 g, (1D) 0.547 g, (2A) 0.532 g, (2B) 0.542 g, (2C) 0.542 g, (2D) 0.536 g. Different amounts of carbon black type N550 (ground with a mortar and pestle and weighed on an analytical microbalance) were added to each filter portion. For each filter, one portion was used as a blank (having no carbon black spike) and the other three portions had carbon black amounts added. The carbon black spike levels were as follows: filter portion (1A) 0 mg, (1B) 5.04 mg, (1C) 9.78 mg, (1D) 15.26 mg, (2A) 0 mg, (2B) 24.90 mg, (2C) 50.04 mg, (2D) 100.14 mg. Each filter portion was placed in a pre-extracted cellulose thimble and the carbon black spike was added to the filter (the mass transferred was weighed by difference). The samples were then covered with pre-extracted glass wool and subjected to a sequential Soxhlet extraction and clean-up as described in Appendix 3. Samples were analysed via GC-MS.

Figure 3.16 (a) illustrates the amount of thiacoronene detected in the dichloromethane extract vs. the mass of carbon black spiked on the air filter. A linear correlation was observed with an R^2 value of 0.996. The toluene data was inconclusive

due to losses of the carbon black spikes within the Soxhlet apparatus during the first extraction with dichloromethane. The experiment was attempted three times, however, in all attempts the fine, loose carbon black spikes passed through the glass wool plugs and were lost to the collection flasks. The dichloromethane data, however, are still very useful in the demonstration of the linearity of carbon black detection using our method, especially since dichloromethane extracts less than 9% of the thiacoronene adsorbed to carbon black in the sequential extraction. The sample handling for both the dichloromethane and toluene extracts was identical.

This experiment indicated that by monitoring levels of thiacoronene extracted from carbon black, we could accurately detect low levels of carbon black in air particulate samples. Detection of carbon black in air particulate using toluene extracts was further evaluated in the extract spike experiment.

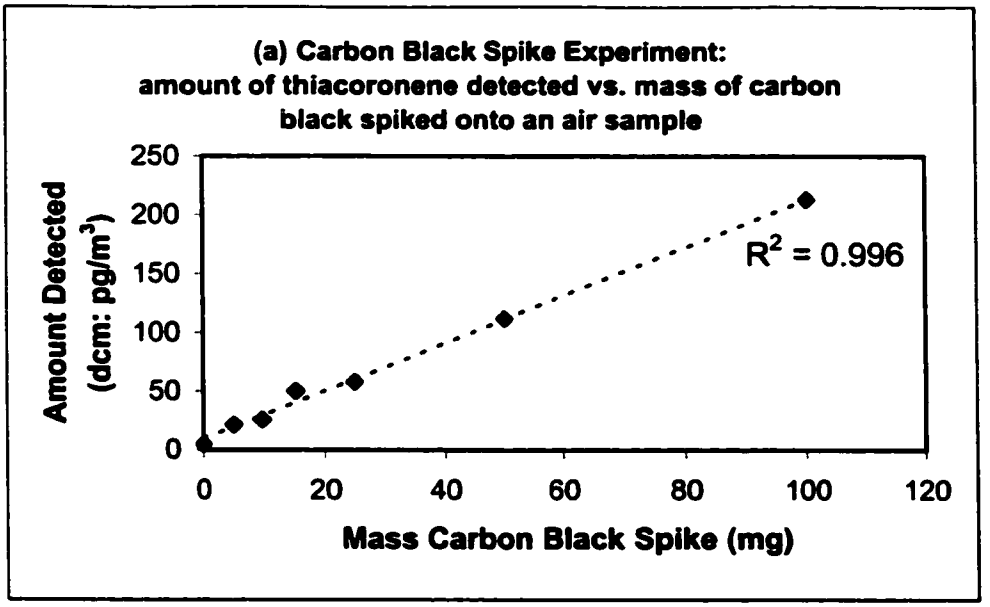
3.6.2.4. The Extract Spike Experiment

In the extract spike experiment, portions of an air particulate extract were mixed with carbon black extract. The subsequent toluene extracts of an urban air sample (an air sample collected at MOE Station 29118 in an area removed from industry, bordering Hwy. 403) and a carbon black sample (N550) were used. Varying amounts of carbon black extract were spiked into constant amounts of the air extract in order to simulate mixtures of air particulate and carbon black. Each spiked sample contained the equivalent of 50 m^3 of air and mass equivalents of carbon black extracted ranging from 0.1 to 4.78 mg of carbon black (which represents a carbon black concentration of 2 - 96

$\mu g/m^3$ in air). Samples containing air extract only (50 m^3) and carbon black extract only (4.78 mg) were also prepared. Samples were analysed via GC-MS.

Figure 3.16 (b) illustrates the amount detected vs. equivalent carbon black injected for thiacoronene in the simulated air-carbon black mixture. A linear correlation was observed with an R^2 value of 0.987. This experiment indicated that by monitoring levels of thiacoronene extracted from carbon black, we could infer the presence of carbon black in subsequent toluene extracts of air.

Looking back at this experiment after having analysed true ambient levels of carbon black in air, the simulated carbon black levels (2 - 96 $\mu g/m^3$) were significantly higher than levels found in ambient air sampled downwind of the carbon black plant (0.01 - 1.4 $\mu g/m^3$). Although the experiment levels of carbon black were not true to the levels found in Hamilton air, the experiment did succeed in evaluating the linearity of detection of carbon black using thiacoronene as a source tracer. The response for thiacoronene, as well as for structurally-related compounds like benzo[ghi]perylene and coronene in carbon black extract was demonstrated to be linear over a 50-fold concentration range using GC-MS.



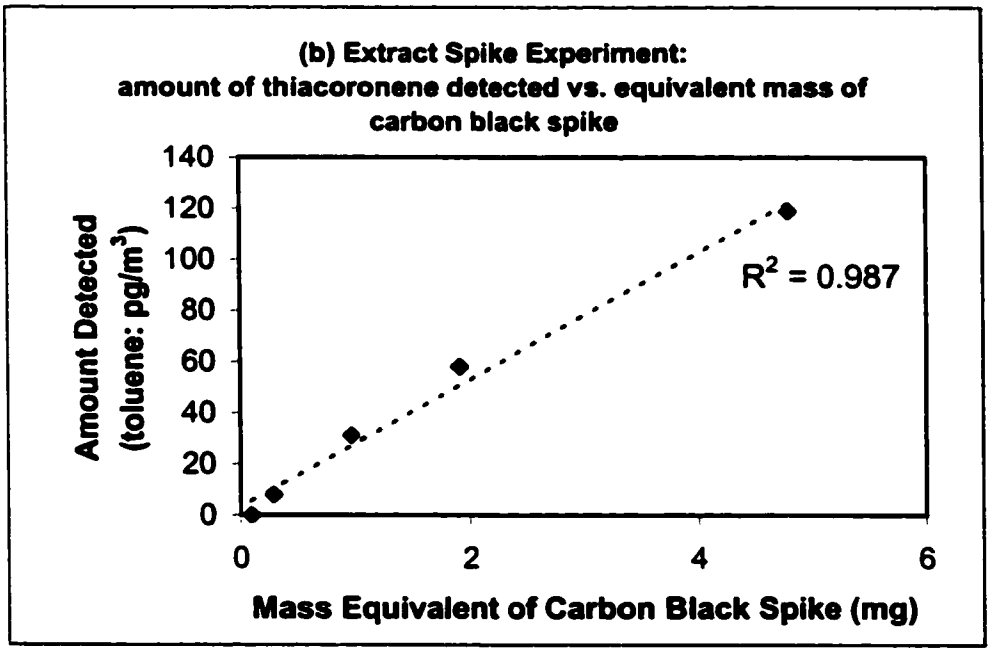


Figure 3.16: (a) Carbon black spike experiment – amount thiacoronene detected vs amount of carbon black spiked onto an air filter sample, (b) extract spike experiment - amount of thiacoronene detected vs. amount of carbon black extract (toluene) spiked into a toluene extract of Hamilton air.

3.6.3. Determination of Carbon Black in Air Using Gas Chromatography with Mass Selective Detection

3.6.3.1. Sample Preparation Methods

The extraction, clean-up and analytical methods used by our research group were evaluated several years ago and have been shown to be applicable to a wide range of environmental matrices including air particulate, sediments, zebra mussels and oils. The details of these procedures are given in previous publications.[37,146,147] In order to increase our speed of clean-up and sample throughput, an open column alumina cleanup was replaced by a silica Sep-Pak cleanup method validated and currently used by the MOE for PAH analysis.[148] The MOE procedure involves a single silica chromatography step using pre-packed, disposable cartridges to remove polar compounds.

Our method also uses a subsequent Sephadex LH-20 clean-up step that is particularly useful in the analysis of trace levels of substituted PAC. Chromatographic cleanup methods have been previously evaluated for (i) open column alumina chromatography, (ii) silica Sep-pak cleanup, (iii) open column alumina chromatography followed by Sephadex LH-20 cleanup, and (iv) silica Sep-pak cleanup followed by Sephadex LH-20 cleanup.[144,149] The chromatographic performance of the silica + Sephadex LH-20 fraction was found to be superior to the silica-only fraction. Several peaks in the chromatogram of the silica-only fraction are not present in the chromatogram of the fraction cleaned up with silica and Sephadex LH-20. These peaks likely included smaller aromatic compounds and other substances that eluted prior to naphthalene from

the Sephadex LH-20 column, but the identities of these peaks were not determined. Gas chromatographic resolution of closely-eluting PAH improved when the Sephadex LH-20 clean-up procedure was employed. The removal of interfering substances was indicated by the flatness of the baseline for the samples that underwent Sephadex LH-20 clean-up.

It was concluded that the Sephadex LH-20 clean-up procedure provided quite an extraordinary clean-up for air particulate samples, leading to a significant improvement in chromatographic performance by GC-MS. It is probable that the maintenance of the GC column and retention gap is reduced and column lifetime increased, when samples are cleaned up using the Sephadex step. While major PAH peaks can be quantified in the silica-only chromatograms, quantitation of minor peaks posed a significant problem. Since thiacoronene is found at trace levels, having peak areas 100-fold to 10000-fold lower than the areas of major PAH peaks, the Sephadex LH-20 step was critical to provide the sensitivity for the analysis and quantification of thiacoronene. Therefore, it was decided to process all sample extracts using the silica + Sepadex LH-20 clean-up procedure.

The majority of the PAC data produced in our research group has been acquired using gas chromatography with mass selective detection (GC-MS operated in selected ion monitoring or full scan modes). Optimization of column temperature gradient, carrier gas flow rate, ion dwell times and time-programmed ion groups was performed for the GC-MS methods used. The column stationary phase used for the separations is DB-17ht (50% phenylmethylpolysiloxane).

3.6.3.2. Determination of an Average Level of Thiacoronene in Carbon Blacks

The thiacoronene concentrations in different carbon blacks vary with their grade. We have found that the concentrations range from 0.002 - 44 μg thiacoronene per gram of carbon black. In order to calculate the average level of thiacoronene in the carbon black potentially released from the carbon black plant over the four year period of air sampling, we consulted with Columbian Chemicals regarding their average production statistics. Approximately one sixth of Columbian Chemical's daily production of carbon black is dedicated to production of the "C" series carbon blacks, and the remaining five sixths of production is dedicated to the production of the "N" and "R" series carbon blacks. Using these statistics on a yearly basis, a weighted average was calculated to approximate thiacoronene levels in carbon black potentially emitted from the plant. This weighted average of 15 μg thiacoronene per gram of carbon black was used as the basic value in the quantification of carbon black in ambient air samples. In the use of this average value (15 μg/g) we have made the assumption that the releases of carbon black from the plant come from general leaks of all carbon blacks made in the entire production system including fugitive emissions from warehouses etc.

In the case that only one type of carbon black was released to the air, such as carbon black R820 (having a thiacoronene concentration of 44 μg/g) we would be overestimating the amount of carbon black released by a factor of approximately 3 using our quantification method. On the other hand, if only carbon black type C7011 was released (having a thiacoronene concentration of 0.0043 μg/g), our method would underestimate

the amount of carbon black released by a factor of approximately 3500. The production of "C" series carbon blacks (high purity carbon blacks produced from coal tar distillate) are not normally produced in plants other than the Hamilton division of Columbian Chemicals, so underestimations on the scale of that for C7011 would not normally be an issue. The majority of carbon black production is focussed on "N" and "R" series used for tire production and other large-scale applications.

In 1998, Columbian Chemicals supplied us with daily carbon black production data logs for only one month's production. We utilized the daily production logs for one month (September, 1997) to illustrate thiacoronene concentration calculations. An example of the calculation of the weighted average level of thiacoronene in the total carbon black produced for one date in 1997 (September 10) are shown in Table 3.6. On September 10, 1997, six types of carbon black were produced. The carbon black types and total masses produced are shown in the table. In addition, the percentages of the total mass of carbon black produced were calculated for use in the weighted average. The "weighted contribution to the overall thiacoronene concentration" was calculated by multiplying the concentration of thiacoronene in each carbon black by the percentage of each carbon black produced. The sum of these values yields the overall thiacoronene concentration (in μg/g) for that date. The corresponding averages for each date in the same month are shown in Table 3.7. Over a 30 day period, there is clear variability in the calculated thiacoronene concentration (range 5.4 – 21.2 μg/g) which depends on the mix of carbon black types made on each date.

In the calculated average in Table 3.7, the number following the symbol ± is the numerical value of the estimated uncertainty of the mean, or an expanded uncertainty $U = ku_c$, with U determined from a standard uncertainty (i.e., estimated standard deviation) u_c = 3.13 μg/g and a coverage factor $k = 2.04$ based on the t-distribution for $\nu = 29$ degrees of freedom. This expanded uncertainty defines an interval within which the unknown value of the standard is believed to lie with a level of confidence of approximately 95 percent. The average concentration of thiacoronene in the carbon black produced in the plant in the month of September 1997 was calculated to be 12 ± 1.2 μg/g. This average is representative of only one month's production, while the average previously calculated for this research (15 μg/g thiacoronene in carbon black) was based on the relative amounts of carbon black types produced at the plant on a yearly basis as quoted by Columbian.

The average weighted thiacoronene concentration used in the carbon black method (15 μg/g) is a more conservative value than the value calculated for the month of September 1997. If we were to use the average weighted thiacoronene concentration for carbon black produced in September 1997 (12 μg/g), our calculated concentrations of carbon black in ambient air would be about 25% higher than those presented in this research.

Table 3.6: Calculation of the overall concentration of thiacoronene in the carbon black produced at Columbian Chemicals Canada Ltd. on September 10, 1997.

Carbon Black Type	Weight Produced (kg)	Percentage Of Total Mass Produced (%)	Concentration Thiacoronene (μg/g)	Weighted Contribution to Overall Thiacoronene Concentration
N650	21818	9.6	9.2	0.89
N220	29892	13.2	10.8	1.42
C1150	27578	12.2	ND	0.00
N660	83234	36.7	14.9	5.47
N299	64229	28.3	17.5	4.96
Total Mass (kg)	226751			
Overall Thiacoronene Concentration (Weighted Average - μg/g) =				12.7

Table 3.7: Thiacoronene concentration in carbon black produced at the carbon black plant, as calculated using Hamilton Operating Statistics Report from Columbian Chemicals Canada Ltd. (September 1997).

Carbon Black Production Dates	Thiacoronene Concentration (µg/g - weighted average)
9/1/97	14.5
9/2/97	11.7
9/3/97	5.4
9/4/97	11.4
9/5/97	9.6
9/6/97	12.6
9/7/97	12.9
9/8/97	9.1
9/9/97	9.3
9/10/97	12.7
9/11/97	13.5
9/12/97	13.2
9/13/97	10.6
9/14/97	10.2
9/15/97	13.5
9/16/97	15.6
9/17/97	15.1
9/18/97	15.1
9/19/97	21.2
9/20/97	14.8
9/21/97	14.5
9/22/97	10.1
9/23/97	8.3
9/24/97	9.3
9/25/97	8.7
9/26/97	8.8
9/27/97	8.1
9/28/97	8.8
9/29/97	11
9/30/97	11.4
Average (Std. Dev.)	12 ± 1.2

3.6.3.3. *Detection of Carbon Black in Selected Hamilton Air Particulate Samples*

The first application of the carbon black method was undertaken using two upwind/downwind pairs of ambient air samples collected in 1995 near the Columbian Chemicals site. Two of the six sampling sites used in our collection of ambient air samples in 1995 (designated as Philip and Gertrude) were located to the west and east of the Columbian Chemicals Canada Inc. property, providing samples upwind and downwind of the site (see Map 4.1). The downwind sampling site, designated as "Philip", was located approximately 300 m. northeast of the carbon black plant and on the roof of a weighscale building on the Philip Environmental property. When the wind blows from the westerly prevailing direction (approximately 230 to 290 degrees from north) the Philip sampling site is downwind of Columbian Chemicals while the Gertrude site which lies 2.7 km to the west is upwind of Columbian Chemicals. The situation is reversed when the wind blows from the east (approximately 50 to 105 degrees from north). The two sets of ambient air samples that were collected downwind of the Columbian Chemicals plant on July 20 and July 23, 1995) were extracted, cleaned-up and analysed for carbon black content.

Substantial levels of thiacoronene were observed in the downwind extracts. Figure 3.17 provides a comparison between GC-MS chromatograms of the subsequent toluene extracts of ambient air samples collected downwind and upwind of Columbian Chemicals and a carbon black sample. A substantial level of thiacoronene (21.5 pg/m^3) is apparent in the sample collected downwind of Columbian Chemicals while the upwind

sample contains a small amount of thiacoronene (0.06 pg/m^3).

The net mass of carbon black collected downwind of the plant was determined by calculating the difference in the upwind and downwind thiacoronene levels divided by the weighted average amount of thiacoronene per gram of carbon black (15 μg/g). The detection limit for thiacoronene using our protocol is 0.06 pg/m^3 (S/N = 3; assuming 2.5 pg thiacoronene injected, 40 m^3 of air injected)) which, if derived solely from carbon black, would correspond to 0.004 μg /m^3 of carbon black in ambient air. The concentrations of carbon black in air we determined are well above that detection limit.

These analyses confirmed that this method was very sensitive and that there were substantial differences between the ambient air samples collected upwind and downwind of Columbian Chemicals. These data were consistent with the presence of carbon black; quantification of the level of carbon black was made possible through comparisons of upwind and downwind data. Calculated levels were 0.24 μg/m^3 of carbon black in the Philip July 20, 1995 sample and 1.43 μg/m^3 of carbon black in the Philip July 23 sample (see Table 3.8).

Figure 3.17: GC-MS total ion chromatograms showing thiacoronene levels in toluene extracts of ambient air collected downwind and upwind of a carbon black plant as compared to a toluene extract of carbon black (top- carbon black, middle - downwind, bottom - upwind)

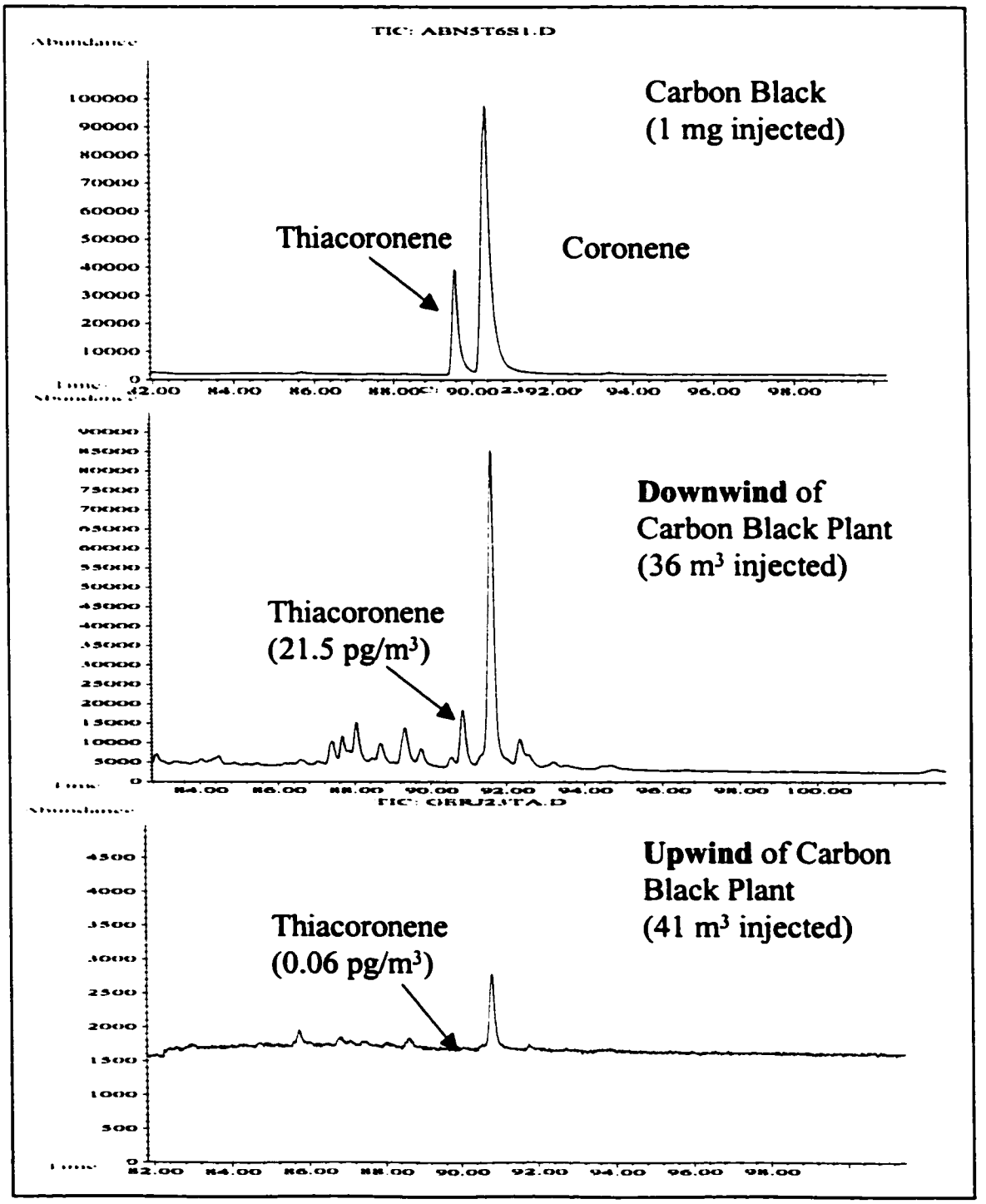


Table 3.8: Determination of carbon black in ambient air collected downwind of a carbon black plant.

Ambient Air Sample (Philip site PM_{10})	**Net Thiacoronene Level** (pg/m^3)	**Calculated Amount of Carbon Black on Entire Air Filter Sample** (mass or % by mass of total particulate collected)	**Calculated Concentration of Carbon Black Particulate in Air** (approximately 100 m from the source)
July 20, 1995	3.54 pg/m^3	0.34 mg or 0.19 %	0.24 $\mu g/m^3$
July 23, 1995	21.5 pg/m^3	2.05 mg or 3.8 %	1.43 $\mu g/m^3$

The current guideline set by the Ontario Ministry of the Environment for the emission of particulate to the air by industries is 25 μg of particulate per m^3 of air at the fenceline. Our results show that the concentration of carbon black found downwind of the carbon black plant about 200 metres beyond the fenceline was well below Ministry guidelines for carbon black emissions. These preliminary results showed that this new analytical methodology was promising. Many more ambient air samples were collected upwind and downwind of Columbian Chemicals over a span of four years and were analyzed in order to evaluate our analytical methodology. A detailed description of the results of this extensive air monitoring campaign for carbon black in air is described in Chapter 4.

3.7. CARBON BLACK METHOD INTERFERENCES

In the carbon black monitoring studies, air particulate filters were collected then selected for extraction and analysis on the basis of wind data obtained during the sampling period. Wind direction and wind speed data were carefully analysed in the sample selection process in order to minimize potential interferences due to coke oven impacts from steel industries. In the assessment of the robustness of our method, the potential interferences due to the steel industry and vehicular impacts were identified and the extent of these interferences was evaluated. A variety of industrial source samples (i.e., steel industry samples, vehicular and coke oven emission samples and road dusts) were used in this evaluation. The levels of thiacoronene in these industrial source samples were determined and chromatographic or spectral interferences in sample analyses were assessed. A more detailed description of these findings can be found in Chapter Five.

3.8. COLUMBIAN CHEMICALS CANADA LTD.: AIR MONITORING CAMPAIGNS 1995-1998

In 1997, Columbian Chemicals Canada Ltd. embarked on a major capital renovation program to improve the environmental performance of the plant on Parkdale Ave. N. in Hamilton. These improvements were designed to significantly reduce the number of plant upsets and the amounts of carbon black and other chemicals released from the plant into the environment. In order to demonstrate that the planned capital expenditures had resulted in improved environmental performance of the plant, our

research group submitted a proposal to Columbian to evaluate the new carbon black methodology and to undertake a program to monitor ambient air quality at locations within communities near the plant. We proposed to determine ambient levels of carbon black in these communities over the course of two years. Columbian Chemicals Canada Ltd. accepted our proposal and funded the current research progam as a research grant.

The proposal included the set up of two inhalable air particulate (PM_{10}) samplers at locations in communities that lie upwind and downwind of the plant and to analyze collected air particulate material on a regular basis. The monitoring protocol can be summarized as follows: (1) samples of inhalable air particulate would be collected at sites in the community, upwind and downwind of the plant; (2) the samples would undergo sequential-extraction and would be analyzed for PAC and for thiacoronene as a source tracer for carbon black; (3) the upwind and downwind data would be compared and the net differences in thiacoronene levels downwind of the plant would be used to determine the ambient levels of carbon black; (4) the levels of metals in these samples would also be determined. Ambient air sampling began in the summer of 1997 and continued in 1998. The sample collection for this air monitoring campaign was described in Chapter Two.

3.9. METHOD DEVELOPMENT CONCLUSIONS

A sequential extraction methodology has been developed for the determination of carbon black in ambient air particulate. Thiacoronene, a 306 Da sulfur-containing PAC and an abundant compound in many carbon blacks, has been proposed as a source tracer

for the determination of carbon black in ambient air. In a preliminary field study, low but easily determined levels of carbon black were detected downwind of a carbon black plant. The detection limit for this method is very low (0.004 μg carbon black per m^3 of air) and the method is well-suited to the sampling and analysis of ambient air.

4. THIACORONENE AS A CARBON BLACK SOURCE TRACER IN URBAN AIR PARTICULATE

4.1. CHAPTER OVERVIEW

Our carbon black method was proposed as a means to monitor any changes in ambient carbon black levels that may have resulted from capital improvements made to Columbian Chemicals between 1996 and 1998. The proposal involved the assessment of this new method for the monitoring of carbon black in communities surrounding Columbian Chemicals. Ambient carbon black data and PAC data spanning four years of air sampling has been acquired in this research project. The levels of carbon black found at different sampling sites, at different distances from the plant in different years were compared.

For a carbon black analysis, each ambient air sample required sequential extraction, affording a dichloromethane extract and a toluene extract. Each extract underwent a two-stage sample clean-up involving elution from a silica Sep-Pak followed by chromatography on Sephadex LH-20. This procedure afforded a non-polar aromatic fraction suitable for GC-MS analysis of PAC and thiacoronene at sub-ppb levels. Quantification of the level of carbon black in each ambient air sample was performed. PAC quantification was performed on both the dichloromethane and toluene extracts of all samples extracted.

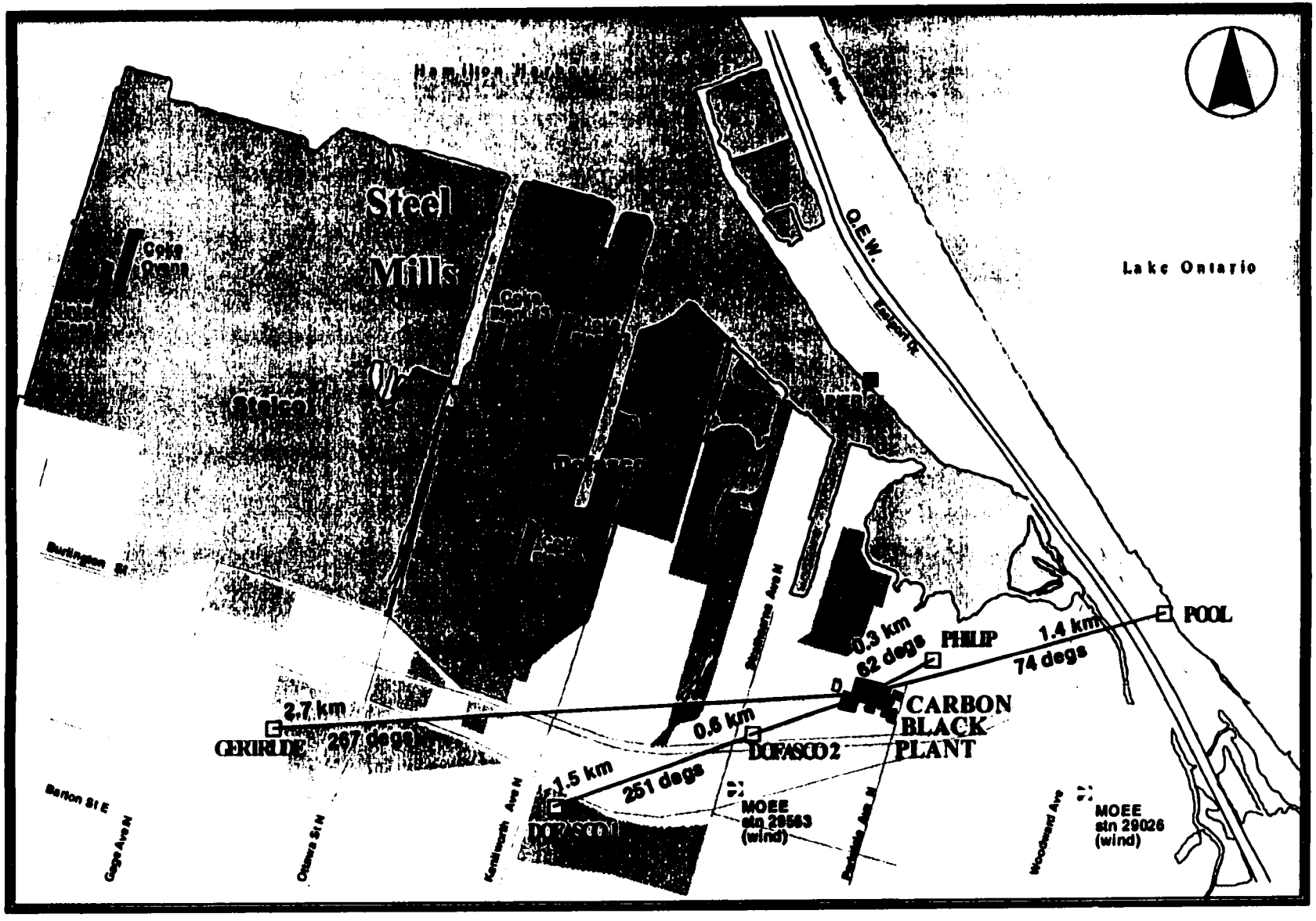
Comparison of the PAC levels in the dichloromethane and toluene extracts provided a unique opportunitiy to compare extraction efficiencies on a large number of environmental samples.

4.2. AMBIENT LEVELS OF CARBON BLACK: 1995 SAMPLING

In the summer of 1995, two ambient air samplers were placed upwind and downwind of the carbon black plant (as described in Chapter 2). The two sampling sites, named Gertrude and Philip, were located 2.7 km upwind and 0.3 km downwind, respectively, from the plant (see sampling locations on Map 4.1). PM_{10} samples were collected for 20 hours per day on consecutive days between July 10 and August 20, 1995 (40 days) at both sampling sites. Hourly wind speed and wind direction data were obtained from the MOE meteorological station (Station 29026) located about 1 km from the Philip site. Examination of this data led to the selection of eight days in which the wind was blowing primarily if not exclusively from the west or southwest, and one date on which the wind was blowing from the northeast. In all but one case, the Philip site was the downwind site. A summary of the air monitoring data including average wind directions with standard deviations and wind speeds is located in Appendix IV.

The levels of thiacoronene and many other PAC in the toluene extracts were determined by GC-MS analysis as described above. The thiacoronene levels upwind of the plant (at the Gertrude site) were very low and ranged from 0.06 to 0.26 pg thiacoronene/m^3 of air, with an average value of 0.12 ± 0.07 pg/m^3 (see Table 4.1).

Map 4.1: Distances and directions from carbon black plant to air sampling sites.



The upwind thiacoronene level at the Philip site was higher, 1.22 pg/m^3, most likely because of the site's proximity to the carbon black plant (300m) and to a loading station for diesel trucks on the Philip Environmental property. The detection limit for thiacoronene under our analysis protocol was 0.06 pg/m^3 (S/N = 3) which, if derived solely from carbon black (at 15 μg/g), would correspond to 0.004 μg/m^3 of carbon black in ambient air. The background (upwind) thiacoronene levels ranged from 1-5 times our detection limit. Thiacoronene levels downwind of the plant were 10 to 100 times higher than upwind levels and ranged from 1.12 to 21.50 pg/m^3 with an average of 8.2 ± 6.4 pg/m^3.

The mass of carbon black collected downwind of the plant was determined by calculating the difference in thiacoronene levels between the upwind and downwind sites (Table 4.1) and dividing by the weighted average amount of thiacoronene per gram of carbon black (15 μg/g). Our results show that concentrations of carbon black about 300 m downwind of the plant in July 1995 varied from 0.06 to 1.43 μg carbon black/m^3 of air. The data for two of the eight upwind/downwind dates (July 23, August 2) exhibited quite high levels of thiacoronene downwind of the plant (> 20 pg thiacoronene/m^3 of air). These high levels were attributed to carbon black and/or potential interferences from steel industry coke oven emissions. Therefore, sample selections in the 1997 and 1998 air monitoring campaigns excluded any sampling periods in which coke oven emissions could potentially impact the air samplers (as determined by hourly wind direction data).

Table 4.1: Determination of carbon black in ambient air sampled 300 m downwind of the carbon black plant (summer 1995).

Sampling Date (1995)	Thiacor.* Level Downwind (pg/m^3)	Thiacor. Level Upwind (pg/m^3)	Net Thiacor. Level (pg/m^3)	Concentration of Carbon Black 300 m Downwind of the Plant ($\mu g/m^3$)
July 14	4.84	0.12	4.72	0.31
July 17	1.12	0.10	1.02	0.07
July 18	6.59	0.26	6.33	0.42
July 19	8.09	0.08	8.01	0.53
July 20	3.64	0.10	3.54	0.24
July 23	21.5	0.06	21.5	1.43
July 29	13.2	0.12	13.1	0.87
**Aug. 2	20.1	1.22	18.9	1.26
Aug. 15	6.97	<0.06	6.97	0.46

(* Thiacoronene, ** Gertrude sampling site is downwind)

After evaluation of the potential impacts of other emissions on the determination of ambient levels of carbon black, we showed that emissions from the steel industries did not appear to interfere with our carbon black method. These findings are described in Chapter 5.

4.3. AMBIENT LEVELS OF CARBON BLACK: 1997 SAMPLING

In the fall of 1997, two ambient air samplers were placed upwind and downind of the carbon black plant at two sampling sites, named Lakeland Pool and Dofasco 1 (as described in Chapter 2). The sites were located 1.4 and 1.5 km respectively, from the plant (see sampling locations on Map 4.1); from the days of sample collection, five upwind/downwind pairs of air particulate samples were selected for extraction and analysis based on analysis of wind data. A summary of the air monitoring data including

average wind directions and wind speeds with standard deviations is located in Appendix IV.

The levels of thiacoronene in the toluene extracts from samples collected upwind of the plant were very low, ranging from 0.06 to 0.98 pg thiacoronene/m^3 of air (see Table 4.2) with an average value of 0.51 ± 0.39 pg/m^3. Thiacoronene levels downwind of the plant were much higher and ranged from 0.32 to 15.17 pg/m^3 and averaged 3.8 ± 6.4 pg/m^3.

These levels were converted into net concentrations of ambient carbon black 1.5 km downwind of the plant and varied from 0.02 to 0.97 μg carbon black/m^3 of air (average = 0.22 ± 0.42 μg carbon black/m^3). One date (September 22, 1997) exhibited a significant impact of carbon black. The company did not report any plant problems or upsets on that date, but the data are consistent with an impact of carbon black at the downwind site, albeit at sub-μg/m^3 levels.

Table 4.2: Determination of carbon black in ambient air sampled 1.5 km downwind of the carbon black plant (fall 1997).

Sampling Date (1997)	Thiacor.* Level Downwind (pg/m^3)	Thiacor. Level Upwind (pg/m^3)	Net Thiacor. Level (pg/m^3)	Concentration of Carbon Black Downwind of the Plant (μg/m^3)
Sept. 4	1.63	0.98	0.65	0.04
Sept. 9	0.32	0.06	0.26	0.02
Sept. 10	0.80	0.17	0.63	0.04
Sept. 22	15.2	0.65	14.5	0.97
Sept. 29 (2 days)	1.10	0.71	0.39	0.03

(* Thiacoronene)

4.4. AMBIENT LEVELS OF CARBON BLACK: 1998 SAMPLING

In the summer of 1998, two ambient air samplers were placed at two sampling sites named Lakeland Pool and Dofasco 2, located 1.4 and 0.6 km respectively, from the plant (see sampling locations on Map 4.1). The Lakeland Pool sampling site was downwind of the carbon black plant when the wind came from 254 degrees from north (also used in 1997), while the Dofasco 2 site was downwind when the wind came from 71 degrees from north. The Dofasco 2 site is located closer to the plant and is near a major truck route in Hamilton's industrial area. This site was the predominant downwind site during this sampling campaign.

The 1998 air sampling campaign started on May 8 and ran continuously until July 10, 1998. A total of forty-three days of air samples were collected at both sampling sites. This sampling period is different from those in 1995 and 1997, which took place mainly between July and September inclusive. Inhalable air particulate loadings at the Dofasco 2 site are significantly higher than at the Pool site. Four of 91 air samples had PM_{10} particulate loadings that exceeded 100 $\mu g/m^3$ of air (see Appendix IV). Based on wind data, air filters from twelve days were identified as being suitable for extraction and carbon black analysis. Thus, the selection involved the extraction of 12 upwind and 12 downwind air particulate samples and required the clean-up and analysis of a total of 48 extracts.

The levels of thiacoronene in the toluene extracts collected upwind of the plant in 1998 ranged from <0.06 to 0.80 pg thiacoronene/m^3 of air, with an average value of 0.20 $\pm$ 0.24 pg/m^3 (see Table 4.3). Thiacoronene levels downwind of the plant ranged from 0.41 to 17 pg/m^3 and averaged 2.3 $\pm$ 4.6 pg/m^3. The standard deviations for these

averages are very large due to the large range of thiacoronene levels observed. The downwind samples always had greater thiacoronene levels than the upwind samples on the same day.

Table 4.3: Determination of carbon black in ambient air sampled 0.6 and 1.4 km** downwind of the carbon black plant (spring 1998).

Sampling Date (1998)	Thiacor.* Level Downwind (pg/m^3)	Thiacor. Level Upwind (pg/m^3)	Net Thiacor. Level (pg/m^3)	Concentration of Carbon Black Downwind of the Plant ($\mu g/m^3$)
May 8	1.83	0.10	1.73	0.12
May 9	1.29	<0.06	1.29	0.09
May 10	0.52	<0.06	0.52	0.04
May 11	0.56	0.22	0.34	0.02
May 13	1.21	0.40	0.81	0.05
May 30	0.46	0.37	0.09	0.01
June 9	1.00	0.34	0.66	0.04
June 11	1.50	0.10	1.40	0.09
June 12**	0.41	<0.06	0.41	0.03**
June 23	1.55	0.80	0.75	0.05
June 29**	0.70	<0.06	0.70	0.05**
July 6	16.8	0.04	16.8	1.12

(* Thiacoronene; ** samples collected 1.5 km downwind of the plant)

The carbon black levels downwind of Columbian Chemicals Canada Ltd. were found to be very low on average (see Table 4.3) and varied from 0.01 to 1.12 μg carbon black/m^3 of air. Except for the high value on July 6, the average concentration of carbon black at the downwind air sampling site was found to be 0.05 ± 0.03 μg carbon black per cubic meter of air sampled (the average including all values was 0.14 ± 0.31 μg carbon

black/m^3). All concentrations of carbon black were well above our method detection limit of 0.004 $\mu g/m^3$.

The carbon black value on July 6 was 1.12 $\mu g/m^3$; this high value must be the result of some fugitive or accidental release of carbon black from the plant. The wind direction on July 6 precludes any coke oven impacts. The July 6, 1998, September 22, 1997 levels (1.12 and 0.97 $\mu g/m^3$ respectively) and July 23, July 29 and August 2, 1995 levels (1.43, 0.87 and 1.26 $\mu g/m^3$ respectively) showed significantly higher carbon black levels downwind of the plant compared to all other days sampled. These data are from samples collected over 20-24 hours. If there were a short-term release of carbon black from the plant, then the ambient concentrations during this event would be significantly higher. For example, if this carbon black were released over a period of one hour, then the ambient concentrations during that hour would be about 24 times greater than the values in Tables 2 and 3. If this scenario were true, then ambient carbon black levels during that one-hour period would likely be in the 20-25 $\mu g/m^3$ range. Shorter-term releases would result in even higher transient ambient levels. From the viewpoint of a local resident, a short-term release is much more visible than a slower, steady release.

4.5. ANALYSES OF RESIDENTIAL AND ENVIRONMENTAL DUSTS

Four dust samples were collected from private homes in the east-end of Hamilton by Columbian Chemicals staff for analysis. These samples were collected as the result of complaints to the company about "black fallout." Following another complaint, samples of black material were collected from surface water in Hamilton Harbour. All samples were

extracted and analysed in order to determine the amount of carbon black present. In addition, inorganic analyses by ICP-MS were performed on these samples.

The levels of thiacoronene found in the four residential dust samples were very low. The amount of carbon black in the samples was calculated assuming all of the thiacoronene was derived only from carbon black; the calculated amounts were converted to concentrations of carbon black in the particulate (in mg/g) and percentages by weight of particulate; these data are listed in Table 4.4.

Table 4.4: Calculated percentages of carbon black in dusts.

Sample	Max. Conc. of Carbon Black (mg/g)	Calculated Percentage of Carbon Black in Sample (by mass)
Dust Sample: May 26, '97 (mass = 1.081 g)	1.2	0.12 %
Dust Sample: June 9, '97 (mass = 0.930 g)	0.8	0.08 %
Window Pane swipes: July 28, '97	n/a	* 0.992 mg carbon black
Dust Sample: Sept. 16, '97 (mass = 0.858 g)	1.7	0.17 %
Dust suspension in water : '98 (m= 0.0276g)	3.4	0.34 %
Dust suspension in water : '98 (m= 0.0580g)	5.7	0.57 %
Dust suspension in water : '98 (m= 0.1170g)	9.1	0.91 %
Dust suspension in water : '98 (m= 0.0328g)	9.6	0.96 %

* The sample weight could not be determined as it was collected on tissues. Only the maximum potential mass of carbon black in the sample (not the percentage) could be calculated.

Carbon black determinations for the first four dust samples listed in Table 4.4 showed that the maximum percentage of carbon black in the samples was less than 0.2% (or less than 1.7 mg carbon black per gram of particulate). The remaining 99.8% of the "black fallout" particulate, if not all of the particulate, must be derived from sources other than carbon black. Similarly, the floating dusts collected from Lake Ontario exhibited

maximum carbon black levels between 0.34% and 0.96% by mass (concentration range 3.4 - 9.6 mg carbon black per gram particulate). The significance of these calculated carbon black impacts in these residential dust samples is further addressed later in Section 5.6.

It should be appreciated that all of these samples were collected and analyzed as a result of complaints by local residents to Columbian Chemicals. Thus, these samples are very valuable in that they are samples which residents felt were representative of "black fallout" and which they thought had been released from operations at Columbian's plant.

4.6. SUMMARY OF AIR MONITORING RESULTS

The following is a summary of the data collected and an interpretation that relates to plant emissions over the four years of air monitoring.

4.6.1. Background Levels of Thiacoronene in Upwind Air Samples

In order to determine whether thiacoronene may be useful as a source tracer for carbon black in ambient air samples, background levels of thiacoronene in urban air must be evaluated. We have compared the levels of thiacoronene in the upwind air samples in all three years of air particulate monitoring. The levels of thiacoronene in the toluene extracts collected upwind of the plant at the Gertrude site in 1995 ranged from 0.04 to 0.26 pg thiacoronene/m^3 of air while the range in 1997 was 0.06 to 0.98 pg/m^3 and in 1998, was from 0.00 to 0.80 pg/m^3. This difference is also expressed in the average values for all three years at the main upwind sites, although more prevalent in the

1995/1997 comparison (1995 (Gertrude): 0.11 ± 0.07 pg thiacoronene/m^3; 1997 (Dofasco1): 0.63 ± 0.34 pg/m^3; 1998 (Pool): 0.24 ± 0.25 pg/m^3, Table 4.5). This discrepancy could be explained by the differing locations of the upwind sampling sites. In 1995, the main sampling site located upwind of the carbon black plant was the Gertrude site, in a residential neighborhood bordering an industrial property, whereas, in 1997/98 the upwind sites were located directly in industrial areas on Dofasco Inc. property. The air samplers on Dofasco property would have much higher potential impacts from other industrial emissions, road dusts and diesel particulates, thereby increasing background levels of thiacoronene in upwind samples.

Table 4.5: Summary of data: ambient air sampled upwind and downwind of a carbon black plant (1995-1998).

Year of Sampling	Range of Thiacoronene Conc. Upwind (in toluene, pg/m^3)	Range of Thiacoronene Conc. Downwind (in toluene, pg/m^3)	Average Thiacoronene Conc. Upwind (pg/m^3)	Average Thiacoronene Conc. Downwind (pg/m^3)
1995	<0.06 - 1.22	1.1 - 21	0.23 ± 0.38	9.6 ± 7.2
1997	0.06 - 0.98	0.31 - 15	0.51 ± 0.39	3.8 ± 6.4
1998	<0.06 - 0.80	0.41 - 17	0.20 ± 0.24	2.3 ± 4.6

In order to assess the thiacoronene levels in background air particulate, we chose to look at samples representative of background urban air. Our definition of background air particulate includes those upwind air samples which have TPAC values less than 2

ng/m^3. This definition of background air has been utilized by our research group as a tool to differentiate background air from that containing particulates with high TPAC values typically emitted by industrial processes in Hamilton. A total of 15 of the 24 upwind air samples fit into this category. The thiacoronene levels in the toluene extracts of these samples ranged from 0 to 0.37 pg/m^3 with an average of 0.12 ± 0.11 pg/m^3. This average background thiacoronene level, if translated to a carbon black equivalent, represents a mere 0.008 μg carbon black per meter cubed of air. Overall, this thiacoronene level associated with background air particulate (0.12 ± 0.11 pg/m^3 or 4.9 ± 4.3 ng/g) is well below the thiacoronene levels found in the toluene extracts of air collected downwind of Columbian; the thiacoronene levels downwind vary between 0.32 to 21.5 pg/m^3 with the majority of levels above 1.0 pg/m^3. Our calculations of ambient carbon black levels are based upon "net" thiacoronene levels which subtracts out the background.

4.6.2. Carbon Black Levels Downwind of Columbian Chemicals

Table 4.6 summarizes our data for carbon black monitoring from the 1995 - 1998 air sampling campaign. Looking at these values, it appears that average releases of carbon black from Columbian Chemicals in 1997 and 1998 have decreased relative to the average releases found in 1995.

Figure 4.1 shows the ambient carbon black levels detected at the sampling sites upwind and downwind of the plant in 1995 (Figure 4.1 (a)), 1997 (Figure 4.1 (b)) and 1998 (Figure 4.1 (c)). These charts illustrate the varying levels detected (in μg carbon black per m^3) as well as the frequency of carbon black impacts in the air downwind of the plant.

Table 4.6: Summary of data: ambient air sampled downwind of a carbon black plant (1995-1998).

Year of Sampling	Average Concentration of Carbon Black Downwind of Carbon Black Plant ($\mu g/m^3$)
1995	0.62 ± 0.47
1997	0.22 ± 0.42
1998	0.14 ± 0.31

The period of sampling in 1995 prior to the plant renovations yielded the highest single carbon black impact as well as the most frequent significant impacts overall. There were also significant impacts in 1997 and 1998, however, the majority of the impacts were low except for those on September 22, 1997 and July 6, 1998. It is, however, difficult to draw a definite conclusion about the reduction of plant emissions over 4 years from these data because the downwind samples were collected at different distances from the plant in each sampling year. The distance between the air sampling site and the emission source is an important factor in air particulate dispersion.

The charts in Figure 4.2 compare the carbon black impacts during all three years of analysis. Chart (a) shows the concentrations of carbon black on a linear scale, while Chart (b) shows them on a logarithmic scale. A higher frequency of relatively high carbon black impacts on a μg carbon black per m^3 basis is seen in 1995. The significance of these detected carbon black impacts is further evaluated in later in Section 5.6, Figure 5.12.

Our data from this three year study show that, except for occasional events, fugitive emissions of carbon black from Columbian Chemicals detected at our sampling sites in

1997 and 1998 are lower compared to the 1995 values. Average ambient carbon black concentrations at our sampling sites and frequency of relatively high carbon black impacts have decreased since the start of the refurbishment of the plant. Our data also show that there were periodic releases of carbon black from the plant in all years of study.

4.6.3. Air Particulate Levels

All air filter samples collected were dried and weighed in order to determine the PM_{10} concentrations for each air sample. In 1995, 80 ambient air samples were collected. The average mass of particulate found in the 1995 samples was 0.091 ± 0.050 g of particulate per sample (20 hours of collection). The average PM_{10} concentration was 61 ± 34 μg per m^3 of air collected. 50 of the 80 samples had particulate concentrations that exceeded 50 $\mu g/m^3$, 8 of which exceeded 100 $\mu g/m^3$.

In 1997, 50 ambient air samples were collected. The average mass of particulate found in these samples was 0.05 ± 0.02 g of particulate per sample (20 hours of collection). The average PM_{10} concentration was 31 ± 13 μg per m^3 of air collected. Six of the 50 samples had particulate concentrations that exceeded 50 $\mu g/m^3$.

In 1998 a total of 91 ambient air samples were collected as 24-hour samples. The average mass of PM_{10} found in these samples is 0.080 ± 0.05 g per sample corresponding to an average PM_{10} concentration of 48 ± 31 μg particulate per m^3; 37 of the 91 samples had PM_{10} concentrations which exceeded 50 $\mu g/m^3$, 4 of which exceeded 100 $\mu g/m^3$.

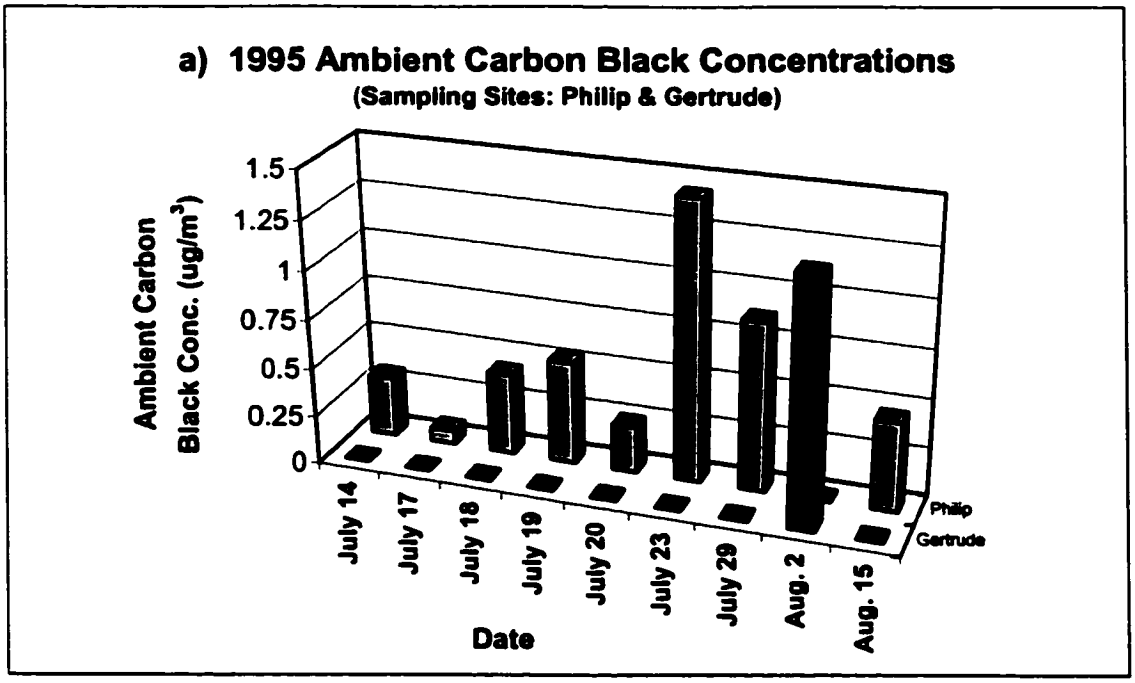
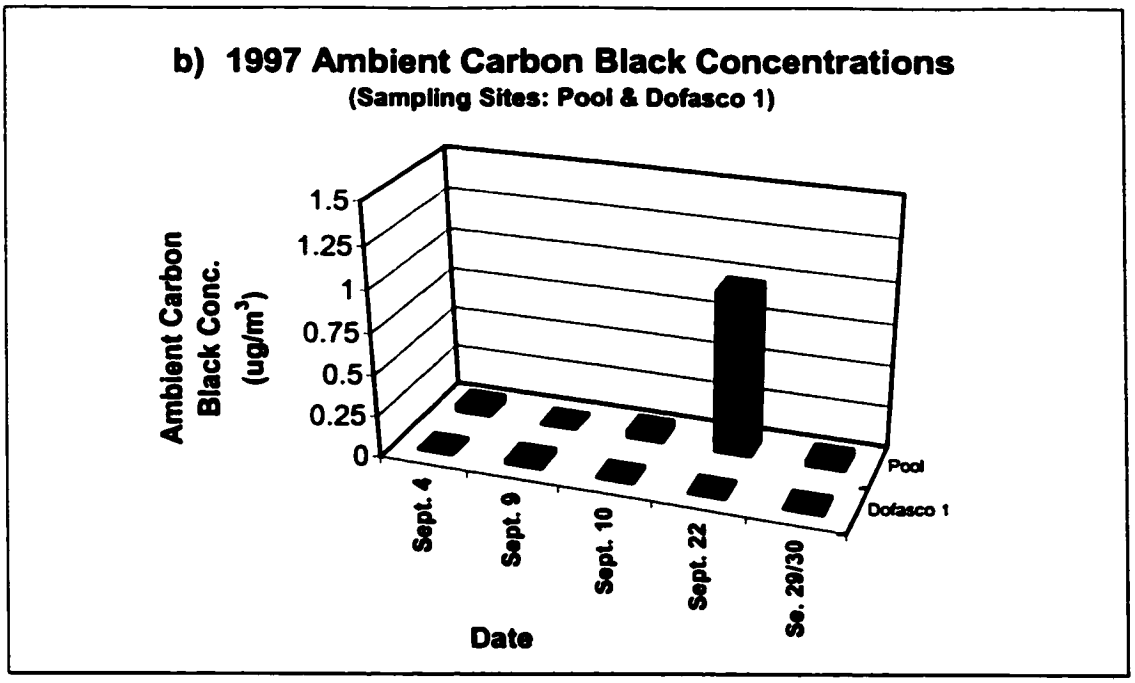


Figure 4.1: Concentrations of ambient carbon black detected at sampling sites in (a) 1995, (b) 1997, and (c) 1998.



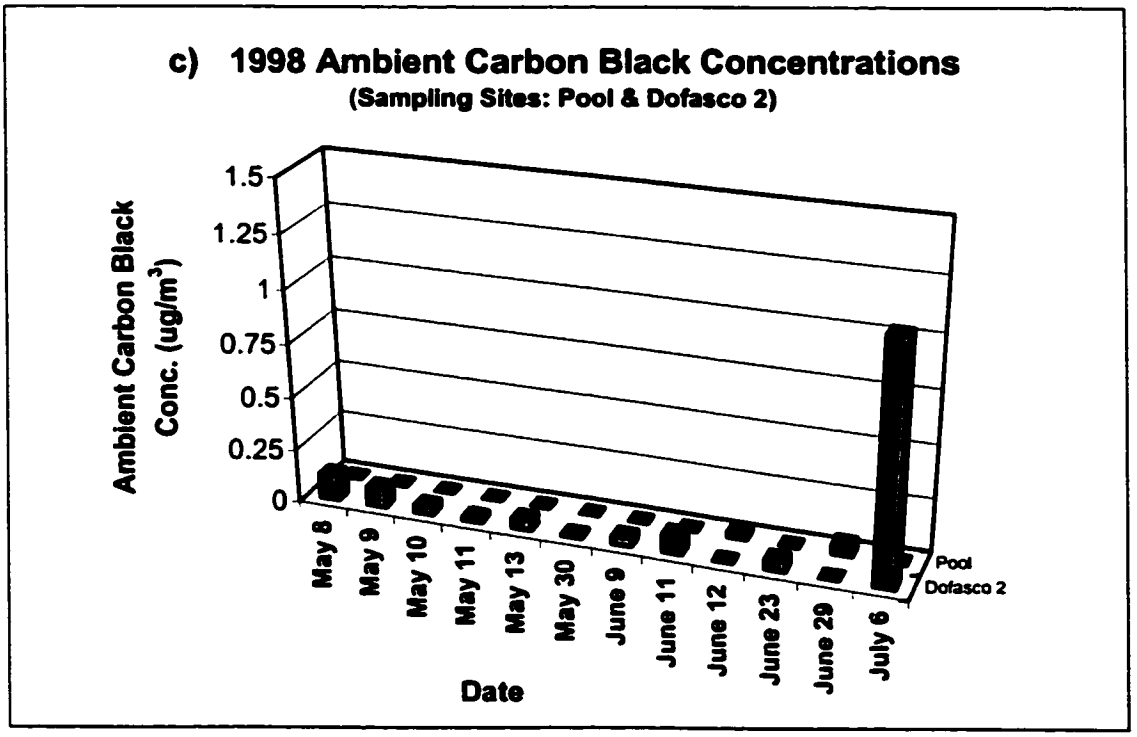


Figure 4.1: Concentrations of ambient carbon black detected at sampling sites in (a) 1995, (b) 1997, and (c) 1998.

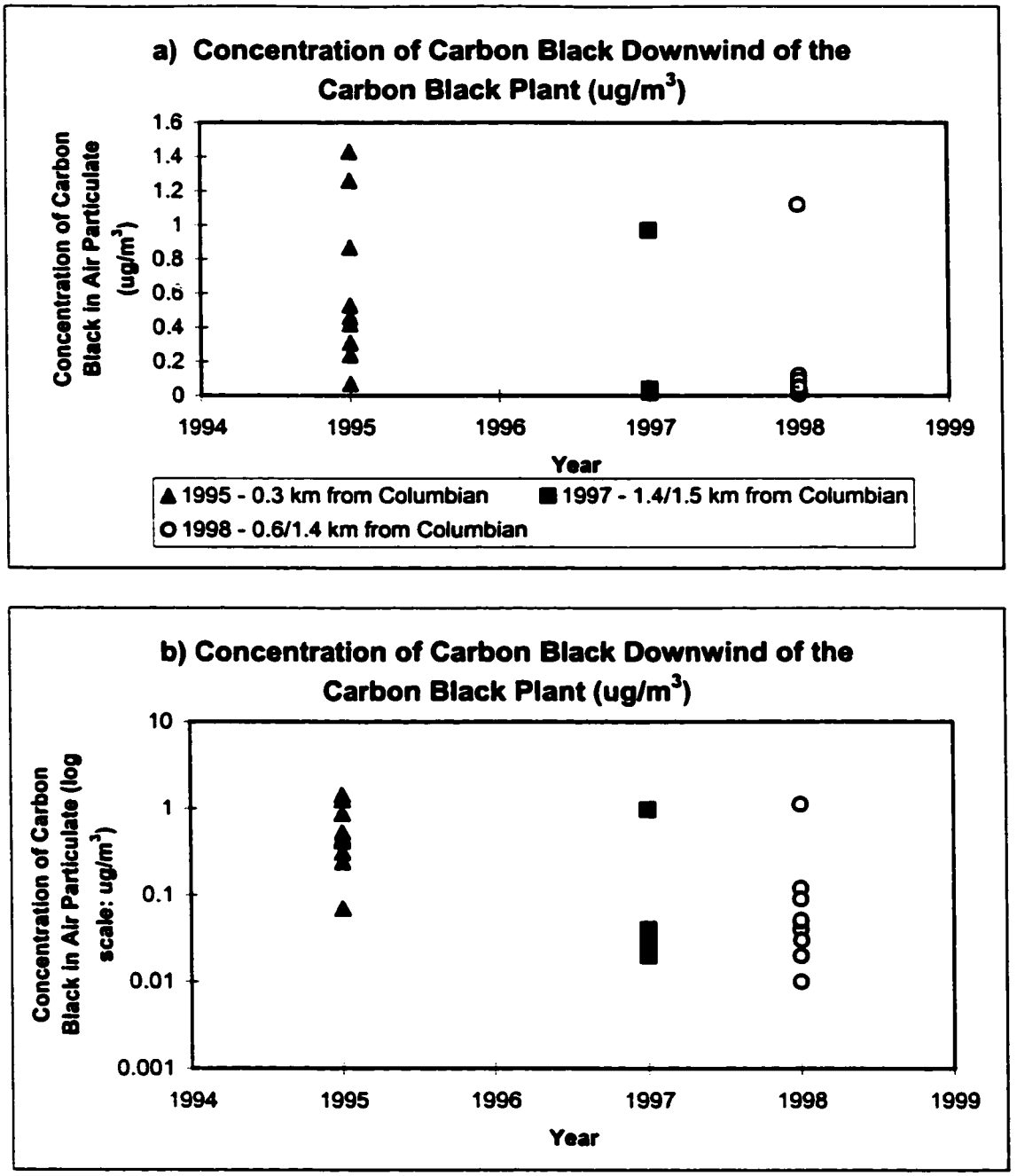


Figure 4.2: Comparison of ambient concentrations of carbon black downwind of a carbon black plant in 1995, 1997 and 1998 on a linear scale (chart a) and on a logarithmic scale (chart b).

During both the 1997 and 1998 sampling periods, the Lakeland Pool site was used. This site lies downwind of a major freeway (the Queen Elizabeth Way). Concentrations of PM_{10} averaged 25 ± 9.0 $\mu g/m^3$ in 1997 (n= 50) and 36 ± 21 $\mu g/m^3$ (n=91) in 1998. The two Dofasco sites (Dofasco1 and Dofasco 2) are in the centre of the industrial area of Hamilton's east end. PM_{10} concentrations in 1997 at the Dofasco 1 site averaged 35 ± 15 $\mu g/m^3$ (n=27) while in 1998 at the Dofasco 2 site the average was 59 ± 34 $\mu g/m^3$ (n=48).

4.7. PAC ANALYSES

A total of 37 PAC were quantified in all sample extracts. These 37 PAC that are listed in Table 4.8 include PAH, a number of thia-arenes, alkylated PAH, quinones, and nitro-PAH. Commonly, only 16 PAH that are classified by the EPA and MOE as "priority PAH" are quantitated in environmental samples. Extra PAC were included in our analysis scheme as some of them pose health concerns (e.g., benzo[c]phenanthrene and dibenzopyrenes), and some are atmospheric transformation products of PAH (e.g., anthraquinone and 2-nitrofluoranthene). Research involving the study of these atmospheric transformation products is beyond the scope of the present thesis, and will be carried out by other students. The levels of the 37 PAC in each sample are located in Appendix VI (in ng/m^3). The "Total Concentration of PAC" in a sample is defined, for the purposes of this thesis, as the sum of the concentrations of the 37 PAC listed in Table 4.8.

4.7.1. Evaluation of Uncertainty of the PAC Determinations

The uncertainty of the PAC determinations for this method was evaluated through the use of between-run precision data for the method recovery of a set of PAC surrogates. It was assumed that these surrogates were representative of the PAC target analytes in our method and that there was no method bias. In our experimental method, a series of three deuterated PAC which had molecular masses chosen as representatives of the entire PAC mass range [phenanthrene-d_{10} (phen.-d_{10}; 188 Da), chrysene-d_{12} (240 Da) and dibenz[a,h]anthracene-d_{14} (DB[ah]A-d_{14}; 292 Da)] were used as recovery surrogates for every air sample analysed (see Appendix III). The recovery of these three surrogates was chosen to be representative of components of uncertainty associated with sample preparation (including extraction and two-stage chromatographic cleanup) and analysis (GC-MS) as these surrogates are added to samples prior to extraction. There was no sample selection involved, as the PAH surrogate recovery data for all air samples analysed in this three-year data set was included in the uncertainty estimations. This uncertainty estimation represents the variability of air sample preparation and analysis over this entire research thesis.

The sample mean (x_i, see Equation 4-1) and the standard uncertainty u_c (estimated standard deviation) associated with the mean for 41 independent observations ($n = 41$, which includes all air samples in the data set analysed in three years: 1995, 1997 and 1998) was calculated. The results of these calculations are in Table 4.7. An expanded uncertainty (U, Equation 4-3) was determined from a standard uncertainty (u_c or in this case $u(x_i)$, see Equation 4-2) and a coverage factor $k = 2.02$ based on the t-distribution for

$\nu = 40$ degrees of freedom, and defines an interval within which the unknown value of the standard is believed to lie with a level of confidence of approximately 95 percent (see the following equations).

$$x_i = \overline{X}_i = \frac{1}{n}\sum_{k=1}^{n} X_{i,k} \qquad (4\text{-}1)$$

$$u(x_i) = s(\overline{X}_i) = \left(\frac{1}{n(n-1)}\sum_{k=1}^{n}(X_{i,k} - \overline{X}_i)^2\right)^{1/2} \qquad (4\text{-}2)$$

$$U = ku_c \qquad (4\text{-}3)$$

Table 4.7: Calculated values for the evaluation of uncertainty in PAC determinations

Calculation	Recovery phen.-d_{10} (%)	Recovery Chrysene-d_{12} (%)	Recovery DB[ah]A-d_{14} (%)
Average (x_i)	50.7	91.6	86.4
Standard Uncertainty (u_c)	7.6	1.4	2.2
Coverage Factor (k) (ν = 40 ; 95% confidence)	2.02	2.02	2.02
Expanded Uncertainty ($U = ku_c$)	15	2.9	4.4

The use of the expanded uncertainty resulting from these calculations is proposed as an approximation of the uncertainty of PAC determinations using our air particulate analysis method. The estimate of uncertainty for the determination of PAC containing 3 rings (or for PAC of similar volatility to phenanthrene-d_{10}; see Compounds 9-15 in Table 4.8) is 15%. The estimate of uncertainty for the determination of PAC containing 4 rings,

as for chrysene-d_{12} (see Compounds 16-34 in Table 4.8) is 2.9%. The estimate of uncertainty for the determination of PAC containing 5 or more rings, as for DB[ah]A-d_{14} (see Compounds 37-53 in Table 4.8) is 4.4%.

The expanded uncertainty calculated for phenanthrene-d_{10} (15%) is larger than that of the higher molecular weight compounds due to its higher relative volatility resulting in greater losses during evaporations steps (evaporation under reduced pressure and under nitrogen evaporating steps). In retrospect, evaporations could have been performed more carefully, using lower temperatures, reduced nitrogen pressure and longer evaporations times in order to achieve higher and less variable recoveries of low molecular mass PAC like phenanthrene-d_{10}.

The expanded uncertainties calculated for chrysene-d_{12} and DB[ah]A-d_{14} (2.9% and 4.4% respectively) represented the uncertainty for mid-to-high mass PAC. This estimation shows that the uncertainty, or error associated with air sample preparation and analysis using this new method was very low (ranging from 3-5% for mid- and high-mass PAC) demonstrating the exceptional quality of the data over this entire research thesis.

The uncertainty for the determination of thiacoronene in the carbon black method is extrapolated to be approximately 5% (based on the calculated uncertainty for DB[ah]A-d_{14}: 4.4%, Table 4.7). This method of evaluating and expressing uncertainty is described in the NIST Guidelines for Evaluating and Expressing Uncertainty (NIST Technical Note 1297) by Taylor and Kuyatt[150] and in other publications.[151,152]

4.7.2. PAC Relationships

The PAC profiles in the dichloromethane and toluene extracts of air sampled upwind and downwind of the carbon black plant were very interesting. For example, total ion current GC-MS chromatograms of the non-polar aromatic fractions (dichloromethane extracts) of air particulate collected upwind and downwind of the carbon black plant on July 18, 1995 are compared in Figure 4.3. The chromatogram from the Gertrude site sample (upwind) was obtained from analysis of an amount corresponding to 40 m^3 of air injected, while the chromatogram of the sample from the Philip site (downwind) corresponds to the injection of 7 m^3 of air. The largest peaks in these complex mixtures correspond to PAH. The peak heights in the downwind sample are about two to four times more intense than peaks in the upwind sample; the corresponding PAC levels are about 20 times more abundant in the downwind sample. The peaks labeled using numbers in the chromatograms are identified in Table 4.8.

Table 4.8: List of PAC quantified in Hamilton air particulate (see chromatogram of calibration standard in Appendix III, Figure A.3.1.).

Peak No.	Compound	Molecular Mass	Detection Limit (pg/m^3)	Detection Limit (ng/g)
9	Dibenzothiophene	184	0.09	0.3
11	Phenanthrene	178	0.1	0.5
12	Anthracene	178	0.1	0.3
13	o-Terphenyl	230	0.2	0.7
14	1-Methylphenanthrene	192	0.2	0.8
15	Anthraquinone	208	0.5	2.0
16	Fluoranthene	202	0.1	0.4
17	Pyrene	202	0.1	0.4
19	m-Terphenyl	230	0.2	0.7
20	p-Terphenyl	230	0.2	0.8
21	Benzo[a]fluorene	216	0.2	0.8
22	Benzo[b]fluorene	216	0.2	0.9
23	Benzo[b]naphtho[2,1-d]thiophene	234	0.1	0.5
24	Benzo[ghi]fluoranthene	226	0.1	0.6
25	Benzo[c]phenanthrene	228	0.2	0.7
26	Benzo[b]naphtho[2,3-d]thiophene	234	0.1	0.5
27	Benz[a]anthracene	228	0.1	0.5
28	Cyclopenta[cd]pyrene	226	0.2	0.7
30	Chrysene	228	0.1	0.5
32	Benzanthrone	230	0.3	1.0
33	2-Nitrofluoranthene	247	0.9	4
34	Benz[a]anthracene-7,12-dione	258	0.5	2.0
37	Benzo[b]fluoranthene	252	0.2	0.7
38	Benzo[k]fluoranthene	252	0.1	0.5
39	Benzo[j]fluoranthene	252	0.1	0.5

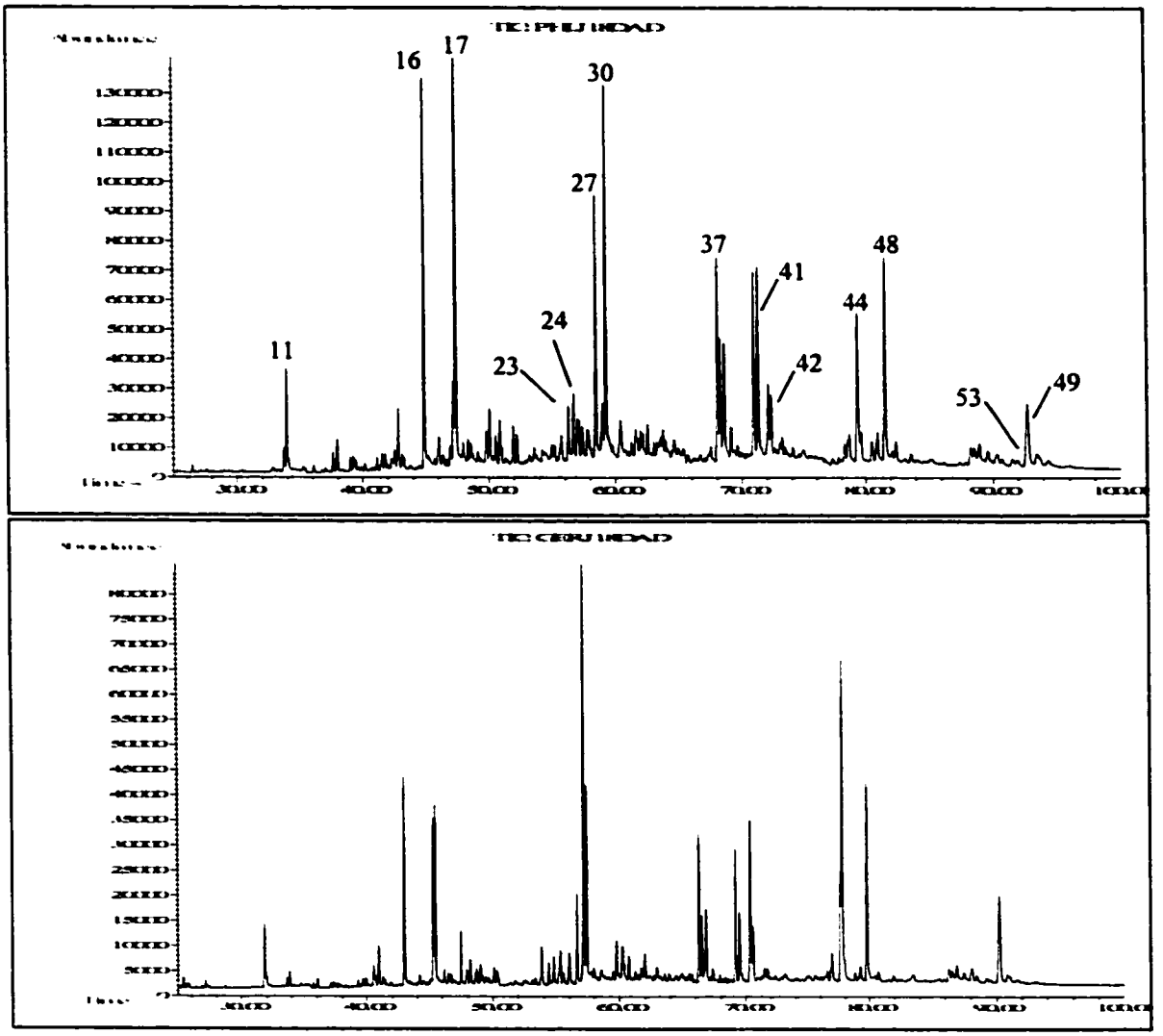
Table 4.8: (continued)

Peak No.	Compound	Molecular Mass	Detection Limit (pg/m^3)	Detection Limit (ng/g)
40	Benzo[e]pyrene	252	0.1	0.6
41	Benzo[a]pyrene	252	0.2	0.7
42	Perylene	252	0.2	0.7
44	Indeno[1,2,3-cd]pyrene	276	0.2	0.7
45	Dibenz[a,c]anthracene	278	0.2	1.0
47	Picene	278	0.2	0.7
48	Benzo[ghi]perylene	276	0.2	0.8
49	Coronene	300	0.2	0.8
50	Dibenzo[a,e]pyrene	302	0.2	0.9
51	Dibenzo[a,i]pyrene	302	0.3	1.0
52	Dibenzo[a,h]pyrene	302	0.4	1.0
53	Thiacoronene	306	0.06	0.3

* The sum of the above PAC was calculated and reported as "total concentration of PAC" or TPAC for each sample

The success of the carbon black method depended entirely on one observation. In the sequential extraction methodology, an initial dichloromethane extraction allowed the removal of almost all of the thiacoronene from other sources of air particulate but little of the thiacoronene derived from carbon black. The subsequent toluene extraction removed the relatively small amount of organics remaining on air particulate, while removing a substantial amount of thiacoronene derived from carbon black.

Figure 4.3: Total ion Chromatograms of non-polar aromatic fractions prepared from the initial dichloromethane extracts of Hamilton air particulate collected on July 18, 1995 (a) downwind of the carbon black plant at the Philip sampling site, 7 m^3 of air equivalent injected and (b) upwind of the carbon black plant at the Gertrude sampling site 41 m^3 of air equivalent injected. Samples were analysed using GC-MS in selected ion monitoring mode. Peak numbers correspond to those in Table 4.8.



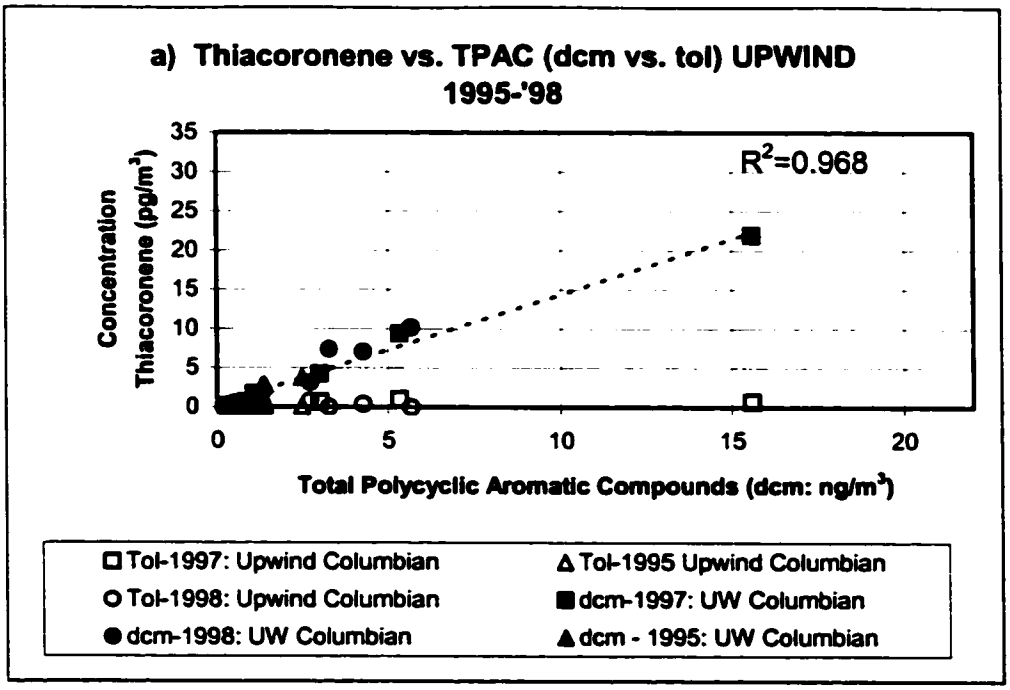
Due to this fundamental difference in extractability of thiacoronene from other air particulate sources versus carbon black, we are able to identify the presence of carbon black in air by looking at the level of thiacoronene in the subsequent toluene extracts of ambient air samples. Since thiacoronene is the basis of our carbon black method, the relationships between the levels of thiacoronene and other PAC were explored. The following pages contain a series of charts plotting the data from all four years of analysis from 1995 to 1998. For 1995, 1997, and 1998 air particulate samples, the "downwind" classification refers to samples which were determined to be downwind of Columbian's carbon black plant. For 1996 samples, the "downwind" classification refers to air sampled downwind of the steel industry coke ovens as indicated on the chart legends.

Figure 4.4 (a) to (c) describes the relationship between the thiacoronene levels in the dichloromethane and toluene extracts of the air particulate samples and their TPAC values. Figure 4.4 (a) contains data for samples collected upwind of the carbon black plant while Figure 4.4 (b) and (c) contain data for samples collected downwind of the carbon black plant. Figure 4.4 (b) is an expansion of the lower left corner of Figure 4.4 c). In Figure 4.4, as TPAC increases, so does the thiacoronene content extracted by dichloromethane. This correlation (R^2=0.968 (chart a) and R^2=0.895(chart b)) was observed for all samples, whether they are upwind or downwind of industry for all four years of sampling (see closed data points representing dichloromethane extracts of samples). A similar relationship is seen for many other PAC in air particulate samples; benzo[b]naphtho[2,1-d]thiophene (B21T) is only one example. In Figure 4.5, the concentration of B21T in dichloromethane is also plotted against TPAC. This relationship

($R^2 = 0.92$) is meaningless in terms of source apportionment of ambient carbon black. The analogous relationship for thiacoronene in the toluene extract is much more useful.

In Figure 4.4 (a), the toluene extracts of the upwind samples (open data points) are congregated low along the x axis exhibiting low TPAC values (range 0.2 to 16 ng/m^3, with most below 3 ng/m^3) and more importantly, low toluene thiacoronene values (range 0 to 0.8 pg/m^3). The toluene extracts of samples collected downwind of the carbon black plant in 1995, 1997 and 1998 (see Figure 4.4 (b)), are found to be scattered through the plot; their thiacoronene content (ranging from 0.3 to 22 pg/m^3) is dependant on their respective impacts of ambient carbon black.

In Figure 4.4 (c), the data for the 1996 samples collected downwind of the steel industry coke ovens were also considered. While the TPAC levels for the steel industry impacted samples range from 30 to 141 ng/m^3 total PAC, the corresponding concentrations of thiacoronene in the toluene extracts never exceed 0.8 pg/m^3. This relationship demonstrates that the thiacoronene content in steel industry emissions is efficiently extracted out in the initial dichloromethane extraction. The potential impacts of steel industry emissions on the carbon black method and the relative extraction efficiency of the dichloromethane verses the toluene extraction is further explored in Chapter 5.



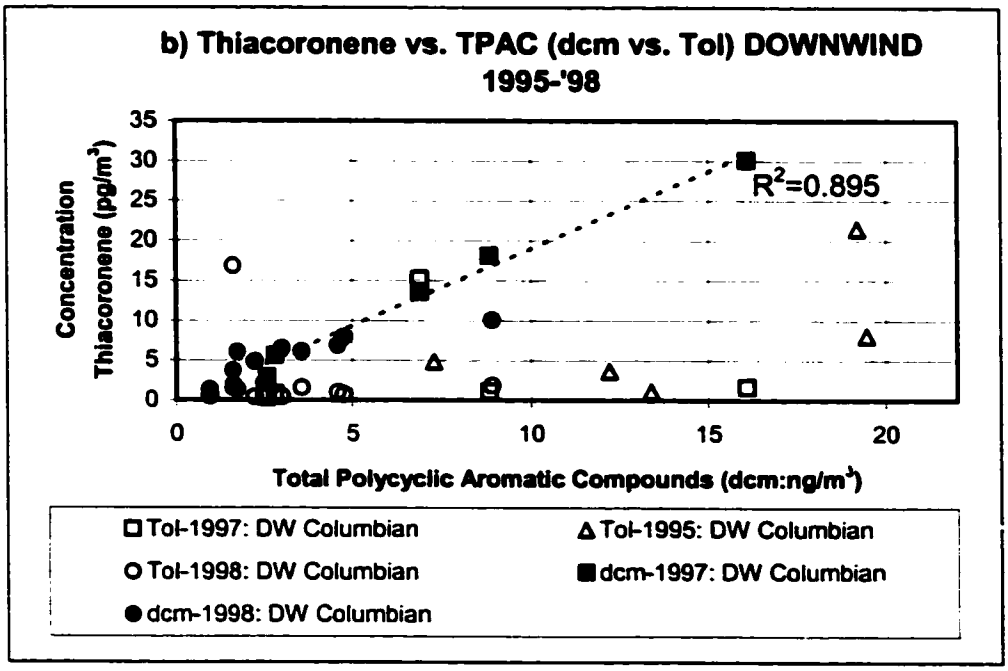


Figure 4.4: Relationship between the concentration of thiacoronene in dichloromethane (closed data points) and toluene extracts (open data points) and the total concentration of PAC in air samples collected a) upwind, (b) downwind of a carbon black plant, and (c) chart b expanded with the x axis on a log scale.

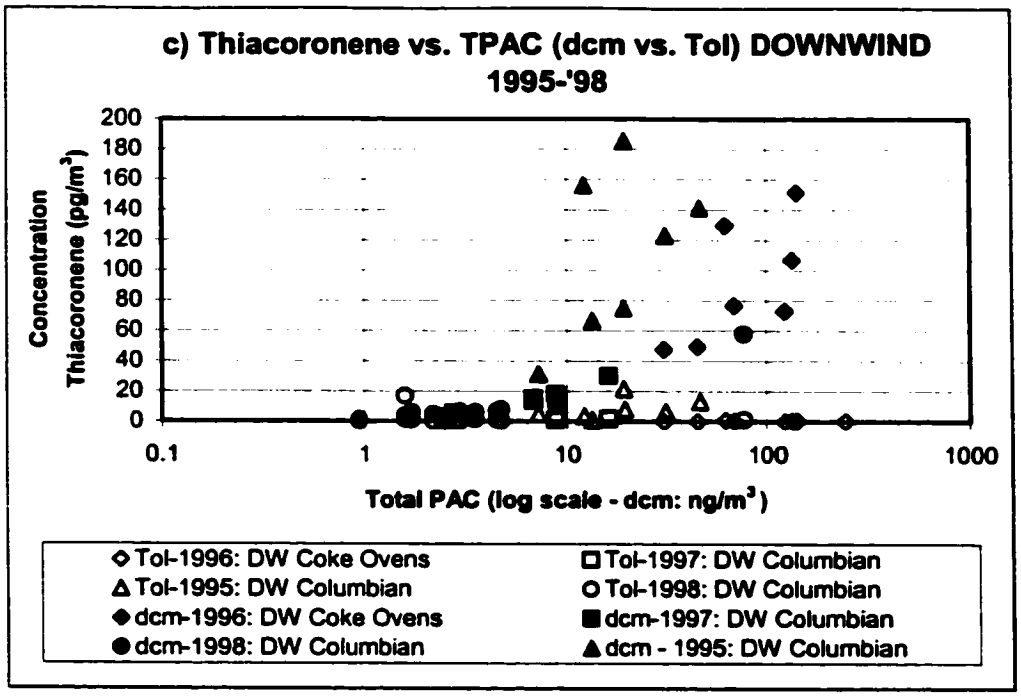


Figure 4.4 (c): Relationship between the concentration of thiacoronene in dichloromethane (closed data points) and toluene extracts (open data points) and the total concentration of PAC in air samples collected downwind of a carbon black plant (x axis on a logarithmic scale). An expansion of 4.4(b).

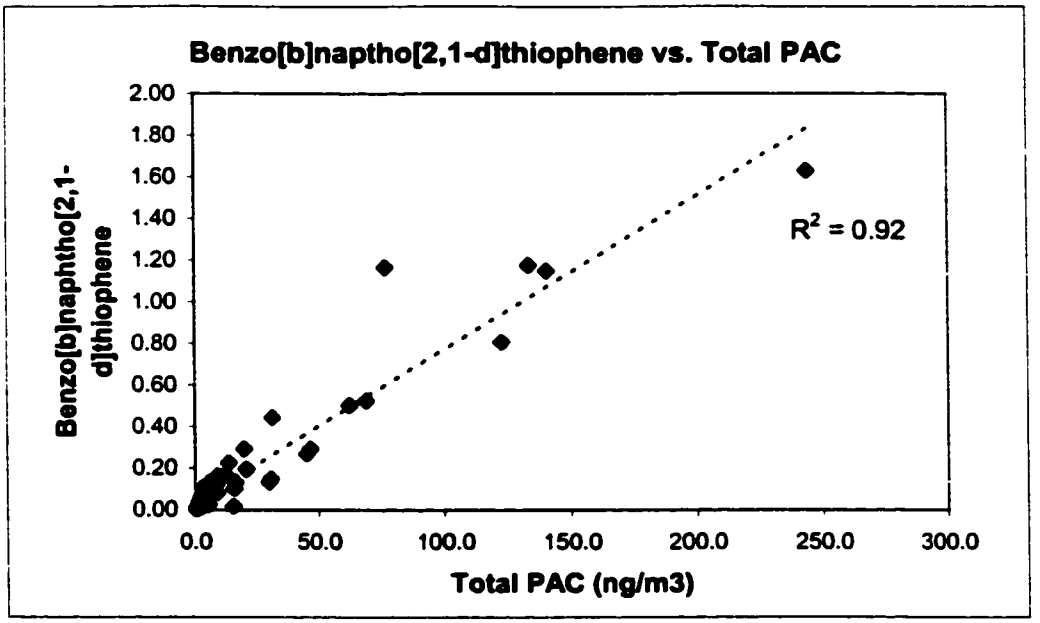


Figure 4.5: Relationship between concentration of benzo[b]naphtho[2,1-d]thiophene and total concentration of PAC in the dichloromethane extracts of ambient air collected in 1995, 1997 and 1998.

5. EVALUATION OF THE CARBON BLACK METHOD USING SOURCE SAMPLES

5.1. CHAPTER OVERVIEW

In the air sampling campaigns that took place in 1995, 1997 and 1998, air samples were selected for analysis based on the potential for impacts by the carbon black plant as assessed by hourly wind direction and wind speed data. In 1995, the prevailing wind direction made Philip the predominant downwind site. Samples collected at Philip were considered to be downwind of the carbon black plant when the average wind direction was between 217 and 267 degrees. Seven sampling days fulfilled these criteria. Since coke plant #1 (Dofasco Inc.) is located 282 degrees relative to the Philip site, the site is considered to be downwind of the coke ovens for sampling periods with average wind directions between 257 and 307 degrees; a range that directly overlaps with the carbon black impact criteria. Consequently, according to the wind direction criteria, 3 of the 7 samples selected from the Philip site had potential impacts from Columbian as well as from Dofasco coke ovens and other steel industry-related emissions. In addition, the Philip site had potential for vehicular and diesel emission impacts, as there was high truck traffic close to the air sampler.

In later years (1997 and 1998), new sampling sites were used and only samples with wind directions that had more than 7 hours of potential impact from the carbon black plant and little likelihood of steel industry impacts were chosen for carbon black analysis. Although our sample selection process in 1997 and 1998 enabled us to minimize potential

interferences from the steel industry, we needed to evaluate whether or not there were any interferences to the carbon black method in all years of sampling, and, if so, the magnitude of these interferences. This was necessary in order to determine the validity of carbon black impacts determined in 1995 as well as to evaluate overall method interferences. The ambient air sampling from the carbon black monitoring campaigns (1995, 1997, 1998) as well as the samples collected to monitor steel industry emissions in 1996 afforded enough samples to properly evaluate the potential interferences, including coke oven emissions, in the carbon black method.

Interferences could include levels of thiacoronene derived from the coking or steelmaking processes, or could include other compounds yielding ions of molecular mass 306 Da during GC-MS analysis. Our source samples aided in the evaluation of these potential interferences. Steel industry emissions, vehicular emissions, coke oven emission samples, industrial road dusts, and other source samples were analysed for thiacoronene concentrations and polycyclic aromatic compounds (PAC) in general.

Further evaluation included the study of the relative extraction efficiencies of dichloromethane and toluene in our sequential extraction method. Extraction efficiencies in terms of relative amounts of PAC extracted by dichloromethane and toluene were compared for air particulate samples and source samples. Our source samples also served in the development of a carbon black threshold; this threshold was designed as a tool for the identification of carbon black impacts in ambient air particulate.

5.2. SOURCE SAMPLES FOR ANALYSIS

We were fortunate in obtaining approximately 60 industrial source samples for this research. These source samples originated from various industries such as Columbian Chemicals Canada Ltd. (providing the samples of carbon black discussed in Chapter 3), Dofasco Inc. and Stelco Inc. who provided baghouse dusts, coals, metallurgical process samples and road dusts. Road dusts collected by the Ministry of the Environment along Burlington street were also provided. These source samples represent most of the major pollution sources in Hamilton, Ontario, including steel industry emissions, carbon black emissions and vehicular emissions. A detailed listing of these industrial source samples may be found in Appendix II of this document.

These source samples originated from the industrial sites we were monitoring, as opposed to the generic reference material samples that are often used as source references. As a result, we are confident that source tracer compounds identified in those samples for source apportionment purposes are representative and applicable to the analysis of ambient air samples collected in the vicinity of the industrial sites. In addition, this number of source samples provides us with a good cross section of the types of particulate contributing to our ambient air samples.

The organic analyses of the source samples required the sequential extraction of each sample with dichloromethane then toluene, a two-stage chromatographic clean-up and GC-MS analysis of each extract. A total of 37 source samples were extracted, providing 74 extracts for cleanup and PAC analysis. A full suite of 37 PAC were quantified in all source sample extracts (PAC data are located in Appendix V). In

addition, the amount of thiacoronene in each source sample was determined in order to assess the potential for interference of each source in the carbon black method.

5.2.1. *Steel Industry Source Samples*

The source samples related to the steel industries may be categorized in the following manner:

(1) coals and cokes

(2) baghouse dusts

(3) process samples derived from outdoor storage piles

(4) slags

(5) miscellaneous process samples

(6) dusts from roads on and surrounding the industrial sites

Those source samples which are most likely to contribute to air pollution, particularly baghouse dusts and process samples derived from outdoor storage piles, were made a priority for organic analysis.

5.2.2. *Air Particulate Samples Containing Coke Oven Emissions*

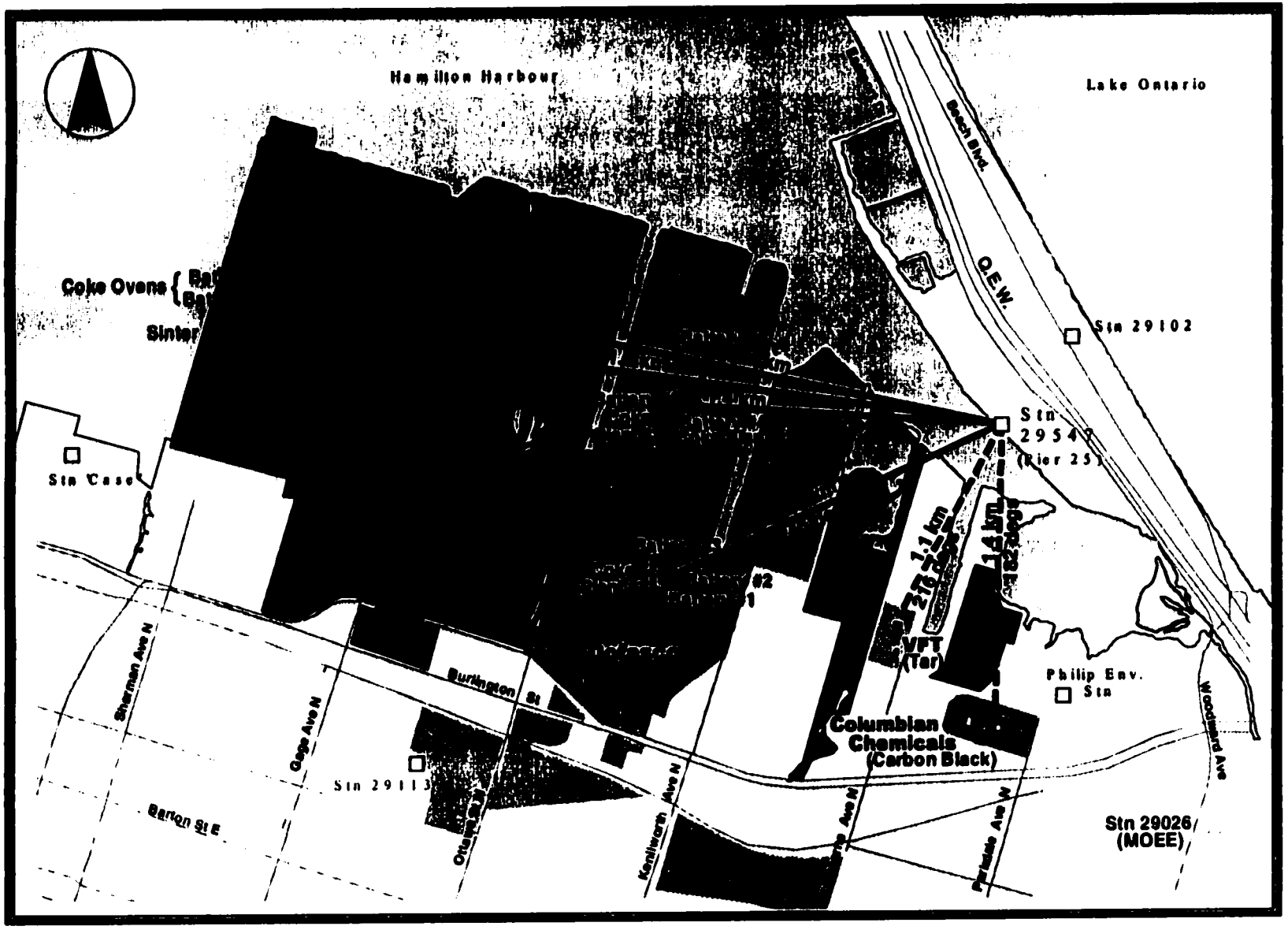
In order to assess the potential interferences of coke oven emissions in the determination of carbon black in ambient air, several ambient air samples known to contain substantial impacts due to coke oven emissions were extracted and analysed. Ambient air samples were collected upwind and downwind of the coke ovens in 1996 at a sampling site located on Pier 25 (see Map 5.1). These samples had been previously

extracted with dichloromethane and analyzed by L. Heydorn; most had thia-arene ratios indicative of coke oven impacts.[153] A selection of eight of these air samples collected downwind of the coke ovens were extracted with toluene. Two air particulate samples collected when Pier 25 was upwind of the coke ovens (i.e., when the wind blew from Lake Ontario) were also extracted and analysed for PAC content.

5.2.3. *Air Particulate Samples Containing Primarily Vehicular Emissions*

Toronto is a large urban centre (population: 2,100,000) with little heavy industry while Hamilton (population: 460,000) has two major steel mills and other associated industries. Pollutant emissions from motor vehicles are widespread in both cities. In order to assess the potential interferences of vehicular emissions in the determination of carbon black in ambient air, several ambient air samples known to contain vehicular emissions were extracted and analysed. Ambient air samples were collected in 1994 at the fenceline adjacent to Highway 404, a six-lane expressway in Toronto.[147] Vehicular emissions (mostly from cars) were expected to dominate these particulate samples. Seven Hwy. 404 air samples were selected for sequential extraction to afford composite extracts.

Map 5.1: Distances and directions from coke oven sources to sampler site at Pier 25.



Diesel Exhaust Particulate Standard Reference Material (SRM 1650, NIST, Gaithersburg, MD) and four diesel exhaust particulate samples provided by Dr. Chung Chiu of Environment Canada were chosen to represent diesel emission sources. The Standard Reference Material (SRM 1650) was selected because other researchers can use this SRM for evaluation of the current work or for comparison to other studies. Standard Reference Materials are also useful for evaluating new or existing analytical methodologies in a laboratory because selected chemical components have been certified by the National Institute of Standards and Technology (NIST). The diesel SRM 1650 was obtained from a single diesel engine only, and profiles of polycyclic aromatic compounds in diesel exhausts depend on the source of fuel, the type of engine and the operating conditions.[75,80]

Four samples of diesel particulate obtained from Environment Canada were extracted and analysed for PAC. These samples were collected between May and July of 1998. The emissions from one vehicle, an Astro Van, were collected on Pallflex filters (Pallflex T60A20). The vehicle ran on a commercially available low-sulfur diesel fuel under different types of driving cycles on each day (as described in Chapter 2). These samples are indicative of modern medium-size diesel engine emissions using current fuels.

5.3. EVALUATION OF POTENTIAL INTERFERENCES OF POLLUTION SOURCES IN THE DETERMINATION OF CARBON BLACK IN AIR

5.3.1. Thiacoronene Levels in the Toluene Extracts of Air Particulate vs. Source Samples

In order to compare ambient air samples, industrial samples and road dust samples, the level of thiacoronene must be expressed in common units such as ng/g (or ppb). In this context the air sample data needed to be converted from pg/m^3 to ng/g particulate; the masses of all particulate samples were available so the calculation was straightforward.

Another issue pertained to detection limits. In the case of the air filter samples the total amount of particulate was only 20-100 mg whereas source samples were extracted in quantities between 0.1 and 6 grams. In the current analytical method, the threshold of detection for thiacoronene in air particulate was 1.9 ng/g or 0.06 pg/m^3 (assuming 2.5% of the total sample or 40 m^3 of air particulate extract is injected, detection limit for thiacoronene: 2.5 pg injected). The detection limit for thiacoronene in the source samples was a little lower than that for air samples and was approximately 0.3 - 1.3 ng/g. This detection limit varied with the mass of extracted particulate (assuming 0.1 - 0.4 g of particulate extracted is in a final volume of 50 μL, detection limit of thiacoronene: 2.5 pg injected).

The levels of thiacoronene in the air and source samples were determined and are listed in Table 5.1 and Table 5.2. Also presented in Table 5.1and Table 5.2 are the values for total concentrations of polycyclic aromatic compounds (TPAC in ppm or μg/g) in

each of the extracts.

It is important to look at thiacoronene levels in a range of potential sources of black fallout for two reasons: (1) to evaluate whether thiacoronene is a good source tracer for carbon black and (2) to evaluate the extent to which other sources may contribute to the "background" level of thiacoronene in air particulate. If thiacoronene truly is a good source tracer for carbon black, the levels of thiacoronene in sources of air particulate other than carbon black must be relatively low in the toluene extracts.

The data in Table 5.1 show that thiacoronene is not present at significant levels in the source samples relative to the levels observed in carbon black. Carbon black has a significantly higher level of thiacoronene (an average level of 15,000 ng/g in the toluene extract) compared to other environmental matrices. The Toronto air composite sample (HWY 404), which is representative of vehicular traffic impacts in urban air, has a comparatively low thiacoronene level (11.8 ng/g). Most of the other source samples have non-detectable thiacoronene levels in their toluene extracts, or very low levels ranging from 0.7 to 20.6 ng/g. No thiacoronene was detected in the toluene extracts of modern diesel particulate samples from Environment Canada, while the highest value, 30.5 ng/g, was found in the diesel exhaust reference material SRM 1650.

Table 5.1: Relative amounts of thiacoronene (ng/g) and total concentration of PAC (µg/g) in source samples.

SAMPLE TYPE Source Samples / Reference Materials	Thiacoronene in DCM (ppb or ng/g)	Thiacoronene in Toluene (ppb or ng/g)	TPAC in DCM (ppm or µg/g)	TPAC in Toluene (ppm or µg/g)
CARBON BLACKS (weighted average value)		**15000**		
CARBON BLACKS (range (see Appendix V))		**<0.3 to 43500**		
N330 (n = 6, dcm; n = 3, toluene)	1330	17300	152	134
N550	184	2095	22.6	13.1
STEEL INDUSTRY SAMPLES (sample name)				
Dofasco Coke Pushing Emissions (do-pem)	15	20.6	95.3	12.6
Stelco Coke Quench Station Deposit (st-cq)	4.54	1.2	19.4	3.84
Coals (do-pin)	< 0.3	< 0.3	7.08	2.39
(st-ca)	< 0.3	< 0.3	14.6	20.1
(do-mas)	< 0.3	< 0.3	14.1	11.3
(do-egu)	< 0.3	< 0.3	8.57	4.44
Coal Breeze (do-cba)	169	4.8	234	11.3
Blast Furnace Dusts (st-db)	< 0.3	<0.3	2.36	none
(st-da)	30.6	2.8	47.3	6.30
Stelco Basic Oxygen Furnace Dusts (st-sp)	< 0.3	< 0.3	0.03	none
(st-sb)	0.3	< 0.3	1.26	0.08
Stelco Sinter Plant Dust Deposits (st-ss)	6.73	1.3	15.1	2.53
Road Dusts (do-d1)	8.14	<0.3	71.4	3.23
(do-d2)	46.6	0.7	100	2.00
(mo-nds)	20.5	2.7	13.8	0.675
(mo-wst)	23.4	< 0.3	29.3	0.778
(mo-phl)	49.5	1.4	9.09	1.43
(mo-wcc)	84.8	1.7	151	6.69
DIESEL EMISSION PARTICULATE (sample name)				
Diesel Exhaust Reference Material -SRM1650 (1650)	60.9	30.5	281	29.2
Vehicular Emissions - HWY 404, 7 days (404gb)	109	11.8	37.8	6.17
Diesel Particulate Samples - Env. Canada (dslshe)	19.6	< 0.3	422	13.4
(dslste)	< 0.3	< 0.3	453	39.4
(dslcbd)	40.6	< 0.3	326	15.9
(dslwvu)	22.7	< 0.3	433	17.0

Table 5.2: Relative amounts of thiacoronene (ng/g) and total concentration of PAC (μg/g) in air particulate extracts.

SAMPLE SET	SAMPLE NAME (site - date)	Thiacoronene in DCM (ppb or ng/g)	Thiacoronene in Toluene (ppb or ng/g)	TPAC in DCM (ppm or μg/g)	TPAC in Toluene (ppm or μg/g)
1996 - Downwind of the Coke Ovens	pier 25 - 04/10/96	5039	2.07	2803	42.8
	pier 25 - 04/16/96	3918	24.3	1885	76.3
	pier 25 - 04/20/96	3006	11.0	3762	57.5
	pier 25 - 04/23/96	3692	12.8	3320	83.5
	pier 25 - 04/26/96	2975	12.6	2767	48.5
	pier 25 - 05/01/96	1499	<0.3	1365	6.68
	pier 25 - 05/12/96	1852	<0.3	1186	69.5
	pier 25 - 05/13/96	1479	<0.3	2486	65.3
Average		2933	12.5	2447	56
standard deviations		1300	8.8	910	24
RSD		43	70	37	43
1995- Downwind of the Columbian Carbon Black Plant	philip - 07/14/95	432	66.5	100	6.72
	philip - 07/17/95	785	13.2	157	3.43
	philip - 07/18/95	783	41.9	199	5.24
	philip - 07/19/95	1931	84.0	202	7.76
	philip - 07/20/95	1246	29.0	97.4	18.1
	philip - 07/23/95	1996	571	510	30.8
	philip - 07/29/95	2779	259	914	26.2
	gertrude - 08/02/95	408	251	372	20.0
	philip - 08/15/95	485	50	167	9.9
Average		1205	152	302	14
standard deviation		850	180	270	10
RSD		70	120	88	69
1997- Downwind of the Columbian Carbon Black Plant	pool - 09/04/97	596	32.3	319	16.7
	dofasco - 09/09/97	90.0	9.71	79.2	19.2
	pool - 09/10/97	187	26.6	93.0	10.3
	pool - 09/22/97	302	338	154	112
	pool - 09/29/97	832	50.5	407	27.0
Average		401	91	210	37
standard deviation		310	140	150	43
RSD		76	150	69	110
1998- Downwind of the Columbian Carbon Black Plant	Dof.2 - 05/08/98	187	34.0	165	11.8
	Dof.2 - 05/09/98	369	78.7	105	7.31
	Dof.2 - 05/10/98	236	95.4	173	23.4
	Dof.2 - 05/11/98	262	69.2	305	22.2
	Dof.2 - 05/13/98	544	11.4	720	5.82
	Dof.2 - 05/30/98	210	14.8	97.2	2.02
	Dof.2 - 06/09/98	200	29.1	134	10.5
	Dof.2 - 06/11/98	52.7	39.9	42.8	16.7
	pool - 06/12/98	167	14.4	77.8	7.20
	Dof.2 - 06/23/98	115	29.4	67.3	8.61
	pool - 06/29/98	122	10.3	73.6	8.30
	Dof.2 - 07/06/98	140	641	61.2	156
Average		217	89	168	23
standard deviation		130	180	190	42
RSD		60	190	110	180

Table 5.2 (continued): Relative amounts of thiacoronene (ng/g) and total concentration of PAC (μg/g) in air particulate extracts.

SAMPLE SET	SAMPLE NAME (site - date)	Thiacoronene in DCM (ng/g part.)	Thiacoronene in Toluene (ng/g part.)	TPAC in DCM or μg/g)	TPAC in Toluene or μg/g)
1996 - Upwind of the Coke Ovens	Pier 25 - 04/12/96	46.5	<0.3	218	46.2
	Pier 25 - 04/14/96	175	<0.3	1770	76.4
Average		**111**		**994**	**61**
standard deviation		**91**		**1100**	**21**
RSD		**82**		**110**	**35**
1995- Upwind of the Columbian Carbon Black Plant	Gert. - 07/14/95	NR	2.74	NR	NR
	Gert. - 07/17/95	112	4.78	54.0	9.82
	Gert. - 07/18/95	83.7	7.54	41.0	5.15
	Gert. - 07/19/95	135	2.82	88.1	2.54
	Gert. - 07/20/95	NR	3.76	24.7	3.30
	Gert. - 07/23/95	NR	2.32	28.1	4.75
	Gert. - 07/29/95	NR	4.58	39.5	12.5
	Philip - 08/02/95	2465	27.3	134	36.4
	Gert. - 08/15/95	NR	<0.3	766	0.0
Average		**699**	**7.0**	**147**	**9**
standard deviation		**1200**	**8.4**	**250**	**12**
RSD		**170**	**120**	**170**	**130**
1997- Upwind of the Columbian Carbon Black Plant	Dof.1 - 09/04/97	249	26.0	142	9.28
	pool - 09/09/97	27.5	2.39	35.5	5.70
	Dof.1 - 09/10/97	100	9.88	64.0	7.97
	Dof.1 - 09/22/97	259	39.5	184	26.7
	Dof.1 - 09/29/97	666	21.4	473	14.7
Average		**260**	**20**	**180**	**13**
standard deviation		**250**	**14**	**180**	**8.4**
RSD		**95**	**73**	**97**	**65**
1998- Upwind of the Columbian Carbon Black Plant	pool - 05/08/98	31.2	2.28	39.3	1.33
	pool - 05/09/98	32.6	<0.3	39.2	0.91
	pool - 05/10/98	38.4	<0.3	48.1	3.44
	pool - 05/11/98	54.3	56.9	94.9	11.1
	pool - 05/13/98	262	16.5	159	5.53
	pool - 05/30/98	75.6	16.8	49.7	3.02
	pool - 06/09/98	145	24.5	95.0	5.88
	pool - 06/11/98	30.2	5.15	39.9	3.60
	Dof.2 - 06/12/98	176	<0.3	78.5	9.81
	pool - 06/23/98	78.6	21.0	69.1	11.6
	Dof.2 - 06/29/98	157	<0.3	87.6	11.2
	pool - 07/06/98	48.4	3.80	46.4	3.62
Average		**94**	**12**	**71**	**5.9**
standard deviation		**74**	**17**	**35**	**4.0**
RSD		**79**	**140**	**50**	**67**

* NR=not reported

The levels of thiacoronene in source and ambient air samples are much lower than levels found in the N and R series carbon blacks which ranged from 2200 to 43200 ng/g. These carbon blacks represent over 80% of carbon black production at the plant. The toluene extracts of all the samples show that the thiacoronene content of all carbon blacks (except the C series blacks) are 100-10,000 times greater than any source or ambient sample examined thus far.

Another way to view the contribution of source samples to the thiacoronene in an air particulate sample is to calculate how much of that source sample would be needed to afford the observed amount of thiacoronene. The greatest amount of thiacoronene observed in any ambient air sample was 30.8 ng; the sample was collected on July 23, 1995 at the Philip site. The mass of particulate collected was 0.054g. Knowing the concentration of thiacoronene in each source sample, the masses of each source required to afford 30.8 ng of thiacoronene in the toluene extract of the air sample are listed in Table 5.3 and illustrated in Figure 5.1.

As calculated, the mass of carbon black in the air sample (July 23, 1995) was 0.0021 grams. The masses of the other source samples required to afford that thiacoronene level ranged from 1.0 to 45 grams. Source samples such as coals and diesel particulate collected by Environment Canada were not included in Table 5.3 because they had non-detectable levels of thiacoronene (<0.3 ppb) in their toluene extracts. Thus for these latter samples the amount of material needed would be >100g. The total mass of particulate collected in that air sample is 0.054 grams; it is impossible for the mass of a source in the air sample to exceed this mass of particulate. Based on these calculations

the masses of source samples needed to account for the thiacoronene observed in air particulate exceeds the observed mass by 19 - 1900 times. Thus, for the sources considered, the thiacoronene detected downwind of the carbon black plant must be derived from carbon black. We therefore conclude that thiacoronene is a useful marker for carbon black in ambient air particulate.

Table 5.3: Mass of source samples required to afford the observed amount of thiacoronene in an air sample collected downwind of Columbian Chemicals Canada Ltd. (Philip Site: July 23, 1995).

Source Sample	Conc. of Thiacoronene in Source Sample (ppb or ng/g)	Mass of Source Sample Required to Afford the Observed Thiacoronene Level in 0.054 g of Air Particulate (g)
Carbon Black	**15000**	0.0021
Coke Pushing	21	1.5
Coke Quench	1.2	26
Coal Breeze	4.8	6.4
Blast Furnace	2.8	11
Sinter Plant	1.3	23
Road Dust – Dofasco	0.7	45
Road Dust – Dofasco/Stelco	2.7	11
Road Dust - Philip	1.4	22
Road Dust – Columbian	1.7	19
Diesel SRM 1650	31	1.0
HWY 404	12	2.6

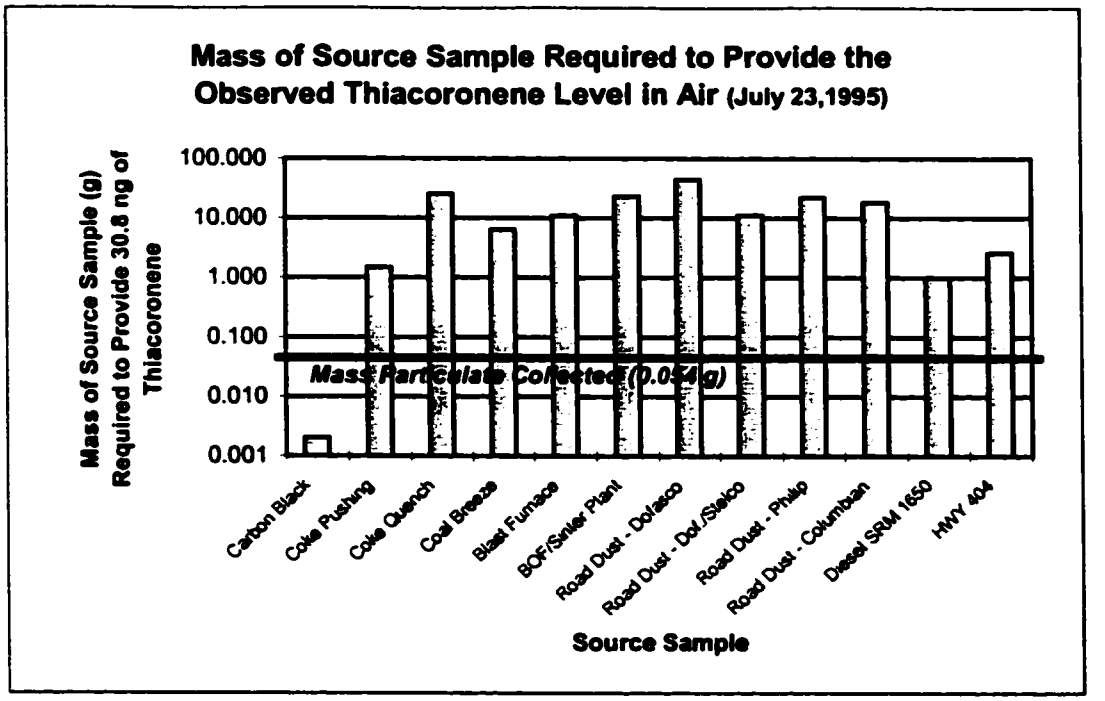


Figure 5.1: The mass of each source sample required to afford the observed net thiacoronene level in the toluene extract of an air sample collected downwind of the carbon black plant on July 23, 1995. (net thiacoronene level: 30.8 ng, total mass of particulate collected = 0.054 g). Note logarithmic scale.

5.3.2. *Evaluation of Background Thiacoronene Concentrations in Ambient Air*

In order to evaluate the extent to which other industrial pollution sources may be contributing to the "background" level of thiacoronene in air particulate, we compared thiacoronene levels in "upwind" air samples to those found in our source samples. Air collected upwind of the carbon black plant is expected to contain low background levels of thiacoronene derived from a range of sources other than carbon black. Thiacoronene levels in the toluene extracts of upwind air particulate ranged from not-detectable (<0.3 ng/g) to 56.9 ng/g (see Table 5.2). Those source samples with the highest levels are most likely to contribute to the thiacoronene background. These samples include diesel exhaust particulate (SRM 1650, 30.5 ng/g), vehicular emissions (Hwy. 404, 11.8 ng/g), coke oven pushing emissions (20.6 ng/g), coal breeze (4.8 ng/g) and possibly road dust samples (<0.3 to 2.7 ng/g) - see Table 5.1. All of these pollution sources, including vehicular emissions and steel industry emissions are probable sources of black particulate in Hamilton.

The thiacoronene levels in all source samples (<0.3 - 30 ng/g) were significantly lower than the averages in the air particulate samples collected downwind of the carbon black plant (average (standard deviation): 1996 - 150 ng/g (200); 1997 - 92 ng/g (140); 1998 - 89 ng/g (180)). These data are also expressed in units relating to the volume of air collected (ng/m^3 or pg/m^3) in Appendix VII.

The thiacoronene levels in the toluene extracts of air samples collected downwind of Columbian ranged from 9.7 to 640 ng/g (Table 5.2); the corresponding levels in the

source samples were much lower, ranging from 0 to 30 ng/g (Table 5.1). Fourteen of the twenty-four downwind samples had thiacoronene level (toluene) higher than SRM1650, the source sample having the highest levels noted thus far (30.5 ng/g). Ten of the downwind samples had levels exceeding 50 ng/g, four of which exceeded 250 ng/g. Almost all of the values found downwind of the carbon black plant could only have arisen from very low but real impacts of carbon black at the sampling site. Furthermore, the upwind average levels of 7, 20 and 12 ng/g thiacoronene (1995, 1997 and 1998 averages respectively; Table 5.2) are in the range of vehicular and diesel source samples.

5.3.3. Evaluation of Other Potential Interferences

In examining the 74 source sample extracts we found no chromatographic or mass spectral interferences which would interfere with our carbon black analytical method. The sequential extraction method provides a very clean toluene extract that is highly selective for the extraction of thiacoronene from carbon black. The dichloromethane extraction removes almost all of the low-mass PAC, a good deal of higher mass PAC, together with many alkylated PAH and heterocyclic aromatic compounds. The two-stage chromatographic cleanup offers a dependable method to separate the analytical target compounds from potentially interfering compounds associated with organic matter and petroleum products (e.g., co-extractive materials including humic acids, oils, fats, aliphatic materials, phthalates and high molecular weight materials not necessarily of interest).

The GC-MS analysis on a DB-17ht column provided excellent chromatographic resolution for similarly eluting compounds like benzo[ghi]perylene, thiacoronene and

coronene. Thiacoronene is easily differentiated from other compounds in the selected ion monitoring mode due to the unusual value of its molecular ion at m/z 306 as well as the ion at m/z 304 formed by loss of H_2. We also monitored for low intensity ions associated with thia-arene fragmentation such as M-32 associated with a loss of the sulfur atom (m/z 274) and the doubly-charged molecular ion (m/z 153).

In selected source sample extracts, we detected two other m/z 306 peaks that elute after thiacoronene. These m/z 306 peaks appear to have no association with carbon black but were found in selected samples associated with vehicular emissions and coking samples. These extra peaks have been found to pose no interference to the carbon black method and are further described in Chapter 7.

5.4. EVALUATION OF THE SEQUENTIAL EXTRACTION METHOD USING SOURCE SAMPLES AND AIR PARTICULATE SAMPLES

In the sequential extraction method each of the samples was extracted twice, first with dichloromethane and second with toluene. For each sample, the amounts of 37 PAC and the total concentration of PAC (TPAC) were determined for both extracts. In Table 5.4 the levels of TPAC determined in the dichloromethane extracts and the toluene extracts of the air samples are compared in terms of relative percentages (see columns titled %TPAC in DCM, %TPAC in TOL). The same data for each of the source samples is compiled in Table 5.5.

5.4.1. *Relative Extractability of TPAC in the Sequential Extracts of Air Particulate*

With respect to the air samples collected upwind and downwind of the carbon black plant, generally, the dichloromethane extract contained about 90% of the TPAC adsorbed to air particulate (see Table 5.4). In two thirds of the air samples analysed, over 90% of the TPAC were found in the dichloromethane extract. This relationship is illustrated in Figure 5.2 (a) where the percentage of TPAC extracted by dichloromethane is plotted against the sum of the total concentration of PAC in both extracts. The same trend was seen for the air particulate samples collected upwind and downwind of the steel industry coke ovens (see 1996 data), where >90% of TPAC were extracted by DCM.

There were, however, only three of the fifty-seven air samples in which the relative amount of TPAC extracted by toluene exceeded 25% of the total; these percentages were 28%, 42% and 72%. These data are also seen in Figure 5.2 a) as labelled points on the graph having low percentages of TPAC in DCM.

The heavily impacted samples collected downwind of the coke ovens were fairly efficiently extracted by dichloromethane (98 ± 1.6%, Table 5.4). Samples with total PAC less than 250 μg/g, which are typical of urban air particulate, showed extraction percentages which ranged from 80 - 100% with many in the 80-90% extracted range (Figure 5.2(a)). These efficiencies are quite high but are well below the quantitative value that many researchers believe that dichloromethane affords. Indeed, as noted above, in three cases the extraction was quite poor. We have looked to the source samples and their relative extraction efficiencies to further evaluate this phenomenon.

Table 5.4: Relative percentages of thiacoronene and total PAC in dichloromethane and toluene air particulate extracts

SAMPLE SET	SAMPLE NAME (site - date)	Percentage Thiacoronene in DCM (%)	Percentage Thiacoronene in Toluene (%)	Percentage TPAC in DCM (%)	Percentage TPAC in Toluene (%)
1996 - Downwind of the Coke Ovens	pier 25 - 04/10/96	100	0.0	98.5	1.5
	pier 25 - 04/16/96	99.4	0.6	96.1	3.9
	pier 25 - 04/20/96	99.6	0.4	98.5	1.5
	pier 25 - 04/23/96	99.7	0.3	97.6	2.4
	pier 25 - 04/26/96	99.6	0.4	98.3	1.7
	pier 25 - 05/01/96	100	0.0	99.5	0.5
	pier 25 - 05/12/96	100	0.0	94.5	5.5
	pier 25 - 05/13/96	100	0.0	97.4	2.6
Average		99.8	0.2	97.5	2.5
standard deviation		0.2	0.2	1.6	1.6
RSD		0.2	110	1.6	65
1995- Downwind of the Columbian Carbon Black Plant	philip - 07/14/95	86.7	13.3	93.7	6.3
	philip - 07/17/95	98.3	1.7	97.9	2.1
	philip - 07/18/95	94.9	5.1	97.4	2.6
	philip - 07/19/95	95.8	4.2	96.3	3.7
	philip - 07/20/95	97.7	2.3	84.3	15.7
	philip - 07/23/95	77.8	22.2	94.3	5.7
	philip - 07/29/95	91.5	8.5	97.2	2.8
	gertrude - 08/02/95	61.9	38.1	94.9	5.1
	philip - 08/15/95	90.7	9.3	94.4	5.6
Average		88.4	11.6	94.5	5.5
standard deviation		12	12	4.1	4.1
RSD		13	100	5.0	86
1997- Downwind of the Columbian Carbon Black Plant	pool - 09/04/97	94.9	5.1	95.0	5.0
	dofasco - 09/09/97	90.3	9.7	80.5	19.5
	pool - 09/10/97	87.5	12.5	90.0	10.0
	pool - 09/22/97	47.2	52.8	57.7	42.3
	pool - 09/29/97	94.3	5.7	93.8	6.2
Average		82.8	17.2	83.4	16.6
standard deviation		20	20	15	15
RSD		24	120	19	93
1998- Downwind of the Columbian Carbon Black Plant	Dof.2 - 05/08/98	84.6	15.4	93.3	6.7
	Dof.2 - 05/09/98	82.4	17.6	93.5	6.5
	Dof.2 - 05/10/98	71.2	28.8	88.1	11.9
	Dof.2 - 05/11/98	79.1	20.9	93.2	6.8
	Dof.2 - 05/13/98	98.0	2.0	99.2	0.8
	Dof.2 - 05/30/98	93.4	6.6	98.0	2.0
	Dof.2 - 06/09/98	87.3	12.7	92.7	7.3
	Dof.2 - 06/11/98	56.9	43.1	71.9	28.1
	pool - 06/12/98	92.1	7.9	91.5	8.5
	Dof.2 - 06/23/98	79.7	20.3	88.7	11.3
	pool - 06/29/98	92.3	7.7	89.9	10.1
	Dof.2 - 07/06/98	18.0	82.0	28.1	71.9
Average		77.9	22.1	85.7	14.3
standard deviation		22	22	19	19
RSD		28	99	23	140

Table 5.4 (continued): Relative percentages of thiacoronene and total concentration of PAC in dichloromethane and toluene air particulate extracts

SAMPLE SET	SAMPLE NAME (site - date)	Percentage Thiacoronene in DCM (%)	Percentage Thiacoronene in Toluene (%)	Percentage TPAC in DCM (%)	Percentage TPAC in Toluene (%)
1996 - Upwind of the Coke Ovens	Pier 25 - 04/12/96	100	0	82.6	17.4
	Pier 25 - 04/14/96	100	0	95.9	4.1
Average		**100**	**0**	**89.2**	**10.8**
standard deviation				**9.4**	**9.4**
RSD				**10.5**	**87**
1995- Upwind of the Columbian Carbon Black Plant	Gert. - 07/17/95	96.3	3.7	84.6	15.4
	Gert. - 07/18/95	91.7	8.3	88.8	11.2
	Gert. - 07/19/95	98.0	2.0	97.2	2.8
	Gert. - 07/20/95	n/a	n/a	91.6	8.4
	Gert. - 07/23/95	n/a	n/a	88.8	11.2
	Gert. - 07/29/95	n/a	n/a	83.6	16.4
	Philip - 08/02/95	98.9	1.1	78.7	21.3
	Gert. - 08/15/95	n/a	n/a	100	0.0
Average		**96.2**	**3.8**	**89.2**	**10.8**
standard deviation		**3.2**	**3.2**	**7.1**	**7.1**
RSD		**3.3**	**84**	**7.9**	**65**
1997- Upwind of the Columbian Carbon Black Plant	Dof.1 - 09/04/97	90.6	9.4	93.9	6.1
	pool - 09/09/97	92.0	8.0	86.2	13.8
	Dof.1 - 09/10/97	91.0	9.0	88.9	11.1
	Dof.1 - 09/22/97	86.8	13.2	87.3	12.7
	Dof.1 - 09/29/97	96.9	3.1	97.0	3.0
Average		**91.4**	**8.6**	**90.7**	**9.3**
standard deviation		**3.6**	**3.6**	**4.6**	**4.6**
RSD		**4.0**	**43**	**5.1**	**49**
1998- Upwind of the Columbian Carbon Black Plant	pool - 05/08/98	93.2	6.8	96.8	3.2
	pool - 05/09/98	100	0.0	97.7	2.3
	pool - 05/10/98	100	0.0	93.1	6.9
	pool - 05/11/98	48.8	51.2	89.6	10.4
	pool - 05/13/98	94.1	5.9	96.6	3.4
	pool - 05/30/98	81.8	18.2	94.2	5.8
	pool - 06/09/98	85.5	14.5	94.2	5.8
	pool - 06/11/98	85.4	14.6	91.7	8.3
	Dof.2 - 06/12/98	100	0.0	88.9	11.1
	pool - 06/23/98	78.9	21.1	85.6	14.4
	Dof.2 - 06/29/98	100	0.0	88.7	11.3
	pool - 07/06/98	92.7	7.3	92.9	7.1
Average		**88.4**	**11.6**	**92.5**	**7.5**
standard deviation		**15**	**15**	**3.7**	**3.7**
RSD		**17**	**130**	**4.0**	**50**

Table 5.5: Relative percentages of thiacoronene and total PAC in dichloromethane and toluene extracts of source samples.

SAMPLE TYPE Source Samples / Reference Materials	Percentage Thiacoronene in DCM (%)	Percentage Thiacoronene in TOL (%)	Percentage TPAC in DCM (%)	Percentage TPAC in TOL (%)
CARBON BLACKS				
N330	7.1	92.9	53.2	46.8
N550	8.1	91.9	63.2	36.8
STEEL INDUSTRY SAMPLES (sample name)				
Dofasco Coke Pushing Emissions (do-pem)	42.2	57.8	88.4	11.6
Stelco Coke Quench Station Deposit (st-cq)	79.1	20.9	83.3	16.7
Coals (do-pin)	ND	ND	75.3	24.7
(st-ca)	ND	ND	38.3	61.7
(do-mas)	ND	ND	55.6	44.4
(do-egu)	ND	ND	66.3	33.7
Coal Breeze (do-cba)	97.2	2.8	95.4	4.6
Blast Furnace Dusts (st-db)	ND	ND	100	0.0
(st-da)	91.7	8.3	88.2	11.8
Stelco Basic Oxygen Furnace Dusts (st-sp)	ND	ND	100	0.0
(st-sb)	100.0	0.0	94.1	5.9
Stelco Sinter Plant Dust Deposits (st-ss)	83.5	16.5	85.7	14.3
Road Dusts (do-d1)	100	0.0	95.7	4.3
(do-d2)	98.5	1.5	98.1	1.9
(mo-nds)	88.3	11.7	95.3	4.7
(mo-wst)	100	0.0	97.4	2.6
(mo-phl)	97.3	2.7	86.4	13.6
(mo-wcc)	98.1	1.9	95.8	4.2
DIESEL EMISSION PARTICULATE (sample name)				
Diesel Exhaust Reference Material -SRM1650 (1650)	66.6	33.3	90.6	9.4
Vehicular Emissions - HWY 404, 7 days (404gb)	90.3	9.7	86.0	14.0
Diesel Particulate Samples - Env. Canada (dslshe)	100	0	96.9	3.1
(dslste)	ND	ND	92.0	8.0
(dslcbd)	100	0	95.4	4.6
(dslwvu)	100	0	96.2	3.8

*ND=not detected

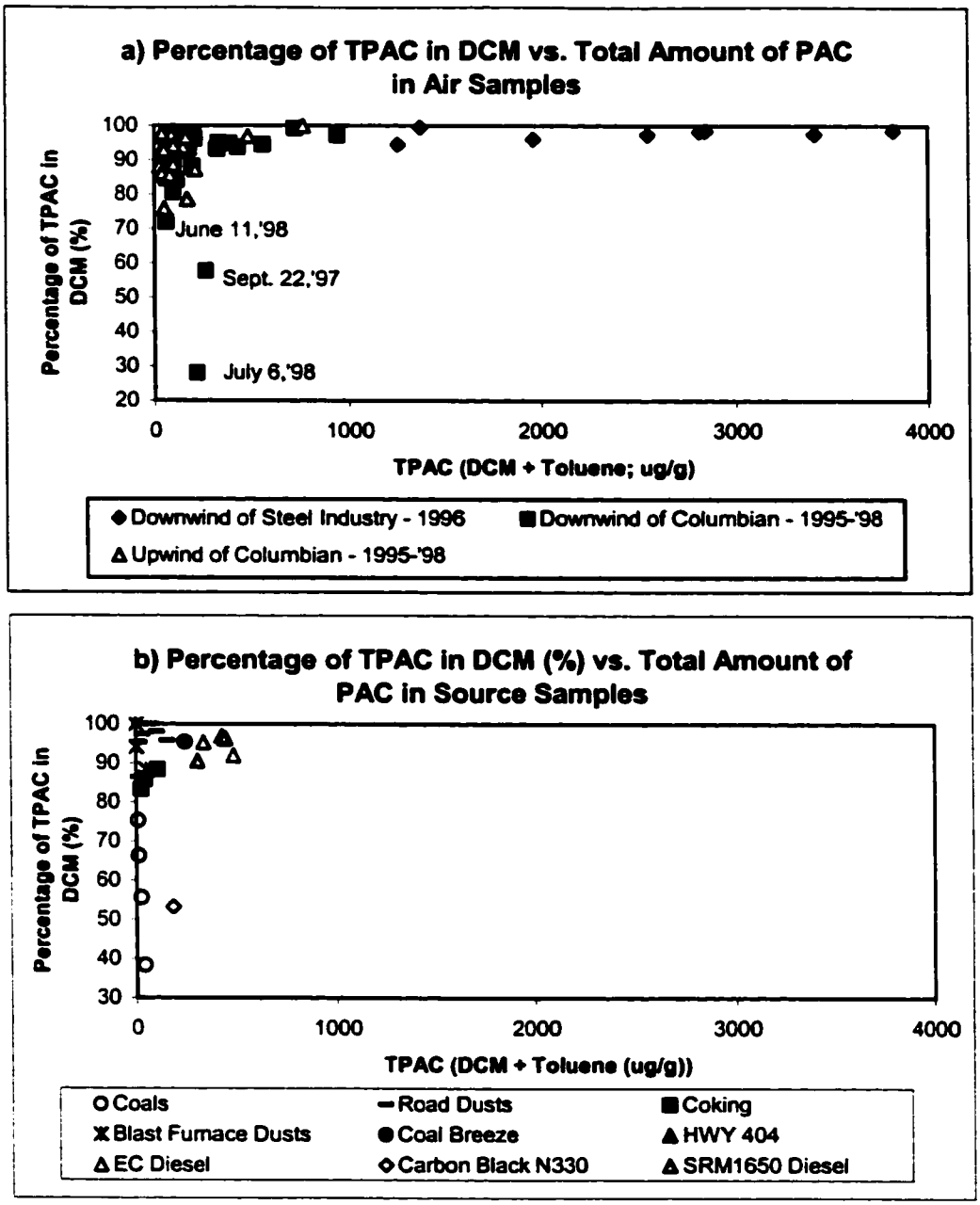


Figure 5.2: Relationship between the percentage of TPAC in dichloromethane vs. total concentration of PAC in both dichloromethane and toluene extracts in a) air samples, and b) source samples.

5.4.2. *Relative Extractability of TPAC in the Sequential Extracts of Source Samples*

Among the source samples, the diesel particulate from Environment Canada, the HWY 404 composite sample and the industrial road dusts all exhibited high TPAC extractability in the initial dichloromethane extraction (i.e., from 86% to 98% of total PAC extracted - see Table 5.5). The steel processing samples including blast furnace dusts, basic oxygen furnace dusts, sinter plant deposits, coal breeze and coke processing samples also behaved similarly, having over 80% of the TPAC extracted initially by dichloromethane (see Figure 5.2 b).

The situation is, however, very different for the coals and the carbon blacks. Of the four coal types extracted, only 38 - 75% of the total PAC on the coals was extracted by dichloromethane (see Table 5.5). For the Stelco coal (ST-CA) over 60% of the total PAC remained on the coal after extraction with dichloromethane. Similarly, for the carbon blacks, the dichloromethane extraction yielded only about 50% of the PAC (see Table 5.5, Figure 5.2 (b)). The relatively low PAC extractabilities observed in three air samples (July 6,'98, Sept. 22,'97 and June 11,'98 - Figure 5.2 (a)) may be due to the presence of coal dust and/or carbon black. The low extractability of PAC from coals and carbon blacks is related to the graphitic chemical structure of coal and carbon black and the lack of other organic compounds as compared to the structures of other particulates.

5.4.2.1. Extractability of PAC on Different Types of Particulate

The majority of polycyclic aromatic compounds adsorbed to air particulate, vehicular emissions, diesel particulate and road dusts (on average 90% of TPAC) are extracted by dichloromethane. This ease of extraction may be explained by the presence of a "liquid coating" on air particulate (as described in Chapter 1). For particles coated with a liquid "organic soup" containing alkanes, aldeydes, ketones, acids, unburned fuels and PAC, one would expect the extractablility of these particles with organic solvents to be fairly facile. For coals and carbon blacks on the other hand, the inherent composition of the particles is much different.

Carbon black is formed during a very inefficient combustion of organic fuels. The microstructure of carbon black particles is composed of parallel planes of carbon ring structures; the planes being oriented around a variety of centers randomly distributed in the particle otherwise known as "growth centres". The graphite-like surface of carbon black has a very strong affinity for polycyclic aromatic compounds, as they are chemically similar in structure.[132]

In coal, the most prominent of the organic molecular groupings is the benzene ring; condensed ring varieties, such as naphthalene, anthracene, and larger ring compounds also are abundant. Clusters formed are believed to be held together by bridges of short aliphatic groups, ether linkages, sulfide and disulfide, and biphenyl type linkages. Oxygen, nitrogen and sulfur are also incorporated into the molecular structure as heterocycles.[154,155] With the

large amount of condensed aromatic structures in coal,[156] one would expect that polycyclic aromatic compounds would be strongly adsorbed to coal, as is the case for carbon black.

In practice, we have seen the strong adsorption of PAC to coal and carbon black expressed by the relatively low DCM extractability (as low as 38% of the PAC extracted by DCM, Table 5.5). This strong affinity of PAC for the inherent chemical structures in coal and carbon black explains the lower relative extraction efficiency of dichloromethane for PAC adsorbed to coal and carbon black (see Figure 5.3(b)).

5.4.3. Relative Extractability of Thiacoronene from Air and Source Samples

The relative extraction efficiency of dichloromethane and toluene for thiacoronene adsorbed to carbon black was discussed in Chapter 3. We showed that the initial dichloromethane extraction yielded little thiacoronene (less than 10%) from carbon black, and that a stronger solvent (i.e., toluene or chlorobenzene) is required to extract the remaining thiacoronene.

The relationship between the percentage of thiacoronene and the percentage of TPAC in dichloromethane extracts of ambient air and source samples is illustrated in Figure 5.3. Among the source samples, the diesel particulate emissions, the HWY 404 composite air sample, the industrial road dust samples, as well as the steel industry coal breeze and furnace dusts all yielded greater than 88% of their thiacoronene content in the initial dichloromethane extraction (see Table 5.5, Figure 5.3 (b)). Compared to the other source samples, the Dofasco coal breeze (DO-CBA) had a high amount of thiacoronene in the dichloromethane extract (169 ppb; 97.2% of the total - Table 5.1). The little that was found

in the toluene extract of DO-CBA (4.8 ppb; 2.8%), however, is fairly insignificant as compared to the values common for carbon black (on the order of 15,000 ppb). The steel industry coals did not yield any thiacoronene in either extraction. The only source sample other than carbon black that yielded a significant proportion of its thiacoronene content in the subsequent toluene extract was the Dofasco Coke Pushing Emissions (DOPEM; see Figure 5.3 (b)). The toluene extract of the coke pushing emissions yielded 58% of the total thiacoronene. Even though the toluene extraction did yield a significant proportion of the thiacoronene from this sample, the coke pushing emissions source does not pose any threat to the carbon black method, as the level extracted was extremely low as compared to those found for carbon black (DO-PEM - 20.6 ppb, average carbon black - 15,000 ppb: Table 5.1).

From our thiacoronene extraction data for the various source samples, we have seen that for most source sample types nearly all of the thiacoronene was easily extracted by dichloromethane. This was also the case for the majority of the air particulate samples (see Table 5.4).

There were a few air particulate samples collected downwind of the carbon black plant, however, for which this was not the case. The air particulate sample collected on September 22, 1997 had only 47% (302 ng/g) of the total thiacoronene extracted by dichloromethane, while the air particulate sample collected on July 6, 1998 had only 18% (140 ng/g) of the total thiacoronene extracted by dichloromethane (see Table 5.4). These two samples had the highest carbon black impacts (0.97 $\mu g/m^3$ and 1.12 $\mu g/m^3$ respectively) that were determined for all ambient samples.

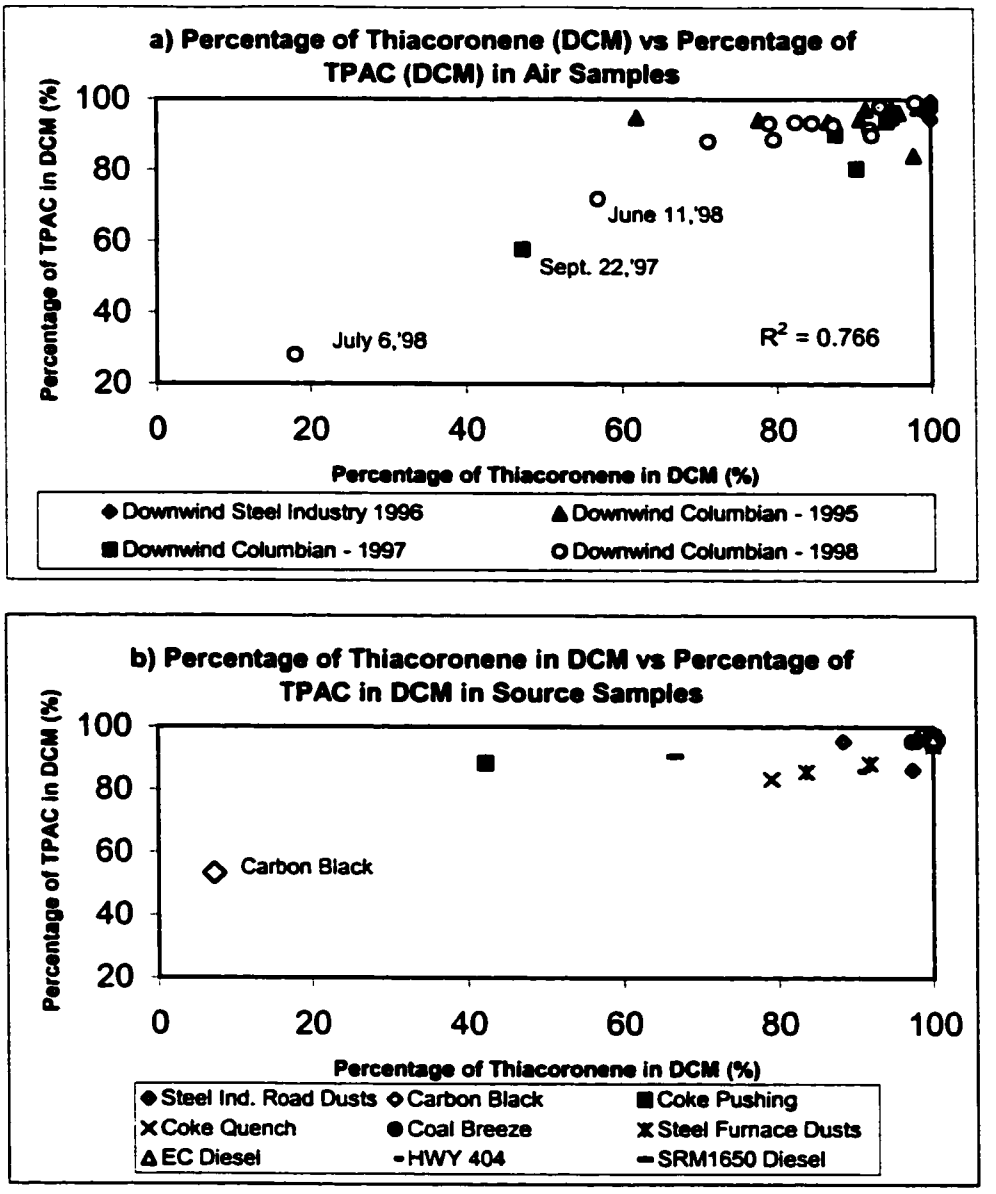


Figure 5.3: Relationship between the percentage of thiacoronene and the percentage of TPAC in the dichloromethane extracts of a) ambient air particulate collected downwind of Columbian and the steel industry and b) source samples.

The low extractability of thiacoronene and PAC (by dichloromethane) for carbon black is illustrated in Figure 5.3 (b). The carbon black data point is found in the lower left of this plot. Similarly, data points for air samples collected downwind of the carbon black plant are found approaching the lower left corner in Figure 5.3 (a). Samples exhibiting carbon black impacts (especially on July 6,'98, Sept. 22,'97 and June 11,'98) appear to exhibit extractabilities closer to those of carbon black than of urban air.

5.4.3.1. Steel Industry Emissions and Relative Extractabilities

A number of the air particulate samples (particularly those from 1996) had rather high thiacoronene levels in the dichloromethane extracts. Six of the air samples collected downwind of the carbon black plant had thiacoronene levels which exceeded 700 ng/g in the dichloromethane extracts. All of these air samples had between 91 - 100 % of their thiacoronene recovered in the dichloromethane extraction (see Table 5.4). These high thiacoronene levels in the dichloromethane extracts are unrelated to the presence of carbon black, as the thiacoronene is too easily extracted; they are undoubtedly derived from coke oven emissions or from some other industrial source.

Air samples collected both downwind of Columbian and downwind of the steel industry in 1995, and downwind of the steel industry in 1996 exhibited PAC extractabilities characteristic of the steel industry source samples and vehicular emissions (80 - 90% of PAC extracted by DCM in: coal breeze, road dusts, steel furnace dusts, EC diesel, HWY 404 etc). These similarities in extractability of thiacoronene and TPAC are more easily viewed in the expanded charts of Figure 5.4 (a) and (b). Although the levels of

thiacoronene in the samples downwind of the coke ovens were quite high, ranging from 1400 to 5000 ppb in the dichloromethane extracts (average (standard deviation) = 2933 ng/g (1300)); the amounts of thiacoronene remaining on the particulate to be extracted by toluene were extremely low, i.e., 0 - 24 ppb (Table 5.2). These odd relative extractabilities for thiacoronene from these coking samples may be related to the way that thia-arenes are produced during the coking process.

5.4.3.2. The Coking Process

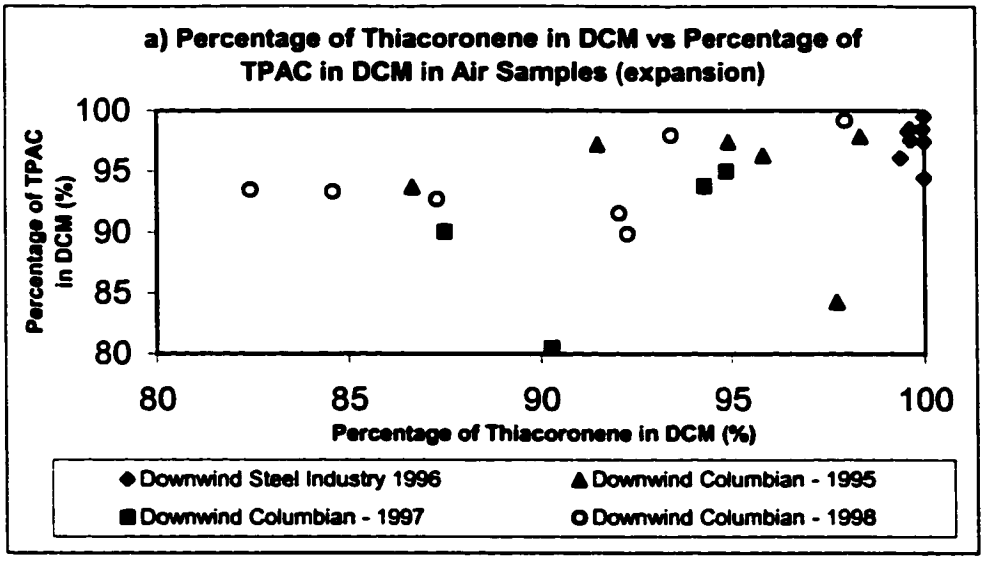
The coking process involves the baking of coal at about 1800 degrees farenheit under reducing conditions to produce coke, a highly carbonaceous residue. The sulfur content of coals may vary from below 1% to more than 10%. Sulfur in coal occurs in three forms: (1) inorganic, (2) organic, and (3) elemental sulfur. The sulfur in coke may be present as sulfide sulfur, SH groups and carbon-sulfur complexes. During the coking process, the sulfur groups also condense and become more aromatic leading to condensed thiophenic rings and aryl sulfides. The volatile sulfur compounds pass into the gaseous products in the forms of hydrogen sulfide, carbon disulfide, COS and mercaptans. Thiophene and its benzologue derivatives (e.g., thiacoronene) are also major components of coke oven emissions.[154-157] The primary gaseous compounds are further altered by temperature and contact with the incandescent coke and oven walls and by contact with other gases from the coal. The variety and amounts of sulfur compounds leaving the system are the overall result of several reactions and equilibria.[144] Approximately 66% of the

inorganic sulfur and 73% of the organic sulfur are retained in the coke; the remainder is released in coke oven gas (the actual distribution depends on the rank of the coal).

As thiophenes are major components of the gases that evolve from the coking process it would be highly likely that thiophenic products like thiacoronene (condensed thiophenic rings or aryl sulfides), along with other PAC, would become condensed on the particulates emitted from the coke ovens or onto particulates already existing in the air.[144] Gaseous thiophenes (like thiacoronene) and other coke oven byproducts that are released to the air and condense onto air particulates would be expected to be easily extracted from the particulates. Our extraction data is consistent with this view; thiacoronene was very easily extracted from air particulate samples containing coke oven emissions, even though its levels on the particulates were very high. Between 99 and 100% of the thiacoronene and 94 - 100% of the total polycyclic aromatic compounds associated with coke oven particulates were readily extracted by dichloromethane (Table 5.4).

5.4.3.3. Other Potential Impacts

Other air samples having relatively high or similar thiacoronene levels in the dichloromethane extracts versus the toluene extracts could be a result of other impacts. Vehicular emissions or some other impact which would add to the thiacoronene load in first extraction using dichloromethane. Vehicular emissions from HWY 404 had thiacoronene levels of 109 ng/g in the dichloromethane extract and only 11 ng/g in the toluene extract (see Table 5.1). Sources like coal breeze also have a higher proportion of thiacoronene extracted by dichloromethane (169 ng/g). Again, this ease of extraction of thiacoronene



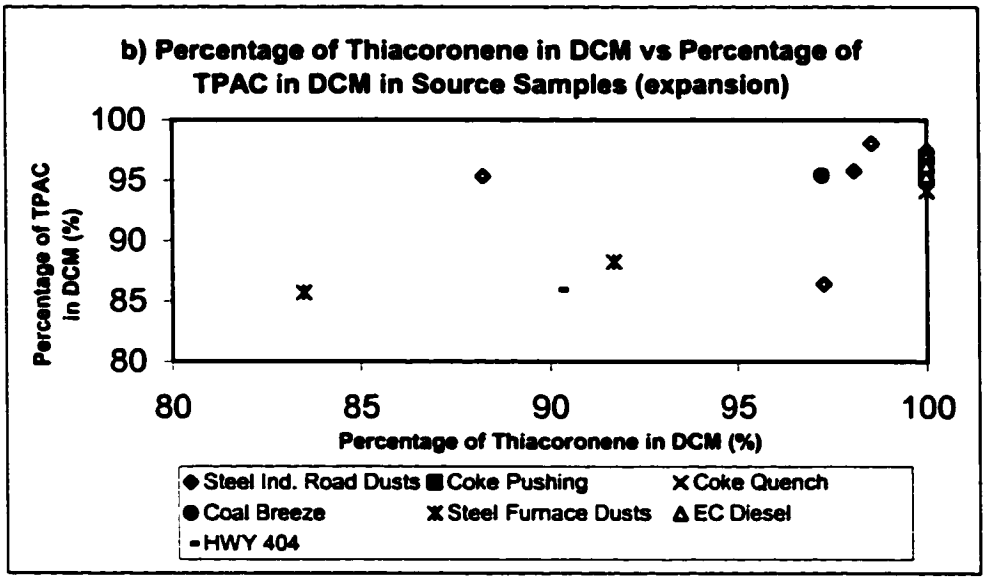


Figure 5.4: Relationship between the percentage of thiacoronene and the percentage of TPAC in the dichloromethane extracts of a) ambient air particulate collected downwind of Columbian and the steel industry and b) Source samples (Expansions of Figure 5.3)

from these particulates may be explained by the low adsorptivity of the thiacoronene on the particulates, perhaps because of the other adsorbed chemicals and the structural properties of these particles. Air particulates coated with organic-based liquids may adsorb emissions from coke ovens, vehicular emissions etc. resulting in a facile extraction of thiacoronene and other PAC with dichloromethane.

5.5. DEVELOPMENT OF A CARBON BLACK THRESHOLD

5.5.1. Evaluation of the Relationship between Total PAC Data and Thiacoronene Data

In Chapter 4, interesting relationships between the TPAC levels and the thiacoronene content of our samples collected upwind and downwind of Columbian were presented. These relationships seemed to be especially useful in the identification of air particulate samples containing carbon black impacts, therefore, were pursued them as a means of developing a "carbon black threshold". This threshold is related to the level of thiacoronene in a sample that enables us to predict that there has been a carbon black impact in air. This section contains a series of figures plotting the data from all four years of analysis from 1995 to 1998 in addition to the data found for the industrial source samples. The figures are set-up in a similar manner as those discussed in Chapter 4, although, they include source sample data.

5.5.1.1. Thiacoronene Extracted by Dichloromethane vs. Total Polycyclic Aromatic Compounds (TPAC)

Figure 5.5 describes the relationship between the thiacoronene levels in the dichloromethane extracts of the air and source samples and their TPAC values. In Figure 5.5 (a) there is a linear trend between TPAC level and the amount of thiacoronene extracted in the initial dichloromethane extractions of air particulate, steel industry samples, diesel particulate samples (denoted as EC diesel), vehicular emissions (HWY 404) and industrial road dusts. Industrial source data, found in the lower left corner and represented by stars, does not include coke oven emissions (represented by diamonds). Both the industrial samples (represented by stars) and the Environment Canada diesel samples (represented by open triangles) were found to have low thiacoronene levels, but higher TPAC values. Figure 5.5 (b) is the same plot as in Figure 5.5 (a), but is an expansion of the lower left corner to provide a better view of low level samples. From this figure we see that our source samples fit well into the trend seen for air particulate in Chapter 4. As TPAC increases, so does the thiacoronene content extracted by dichloromethane. This correlation is not as evident for the Environment Canada diesel samples that have high TPAC levels (320-450 ppm) and thiacoronene levels in dichloromethane below 40 ppb.

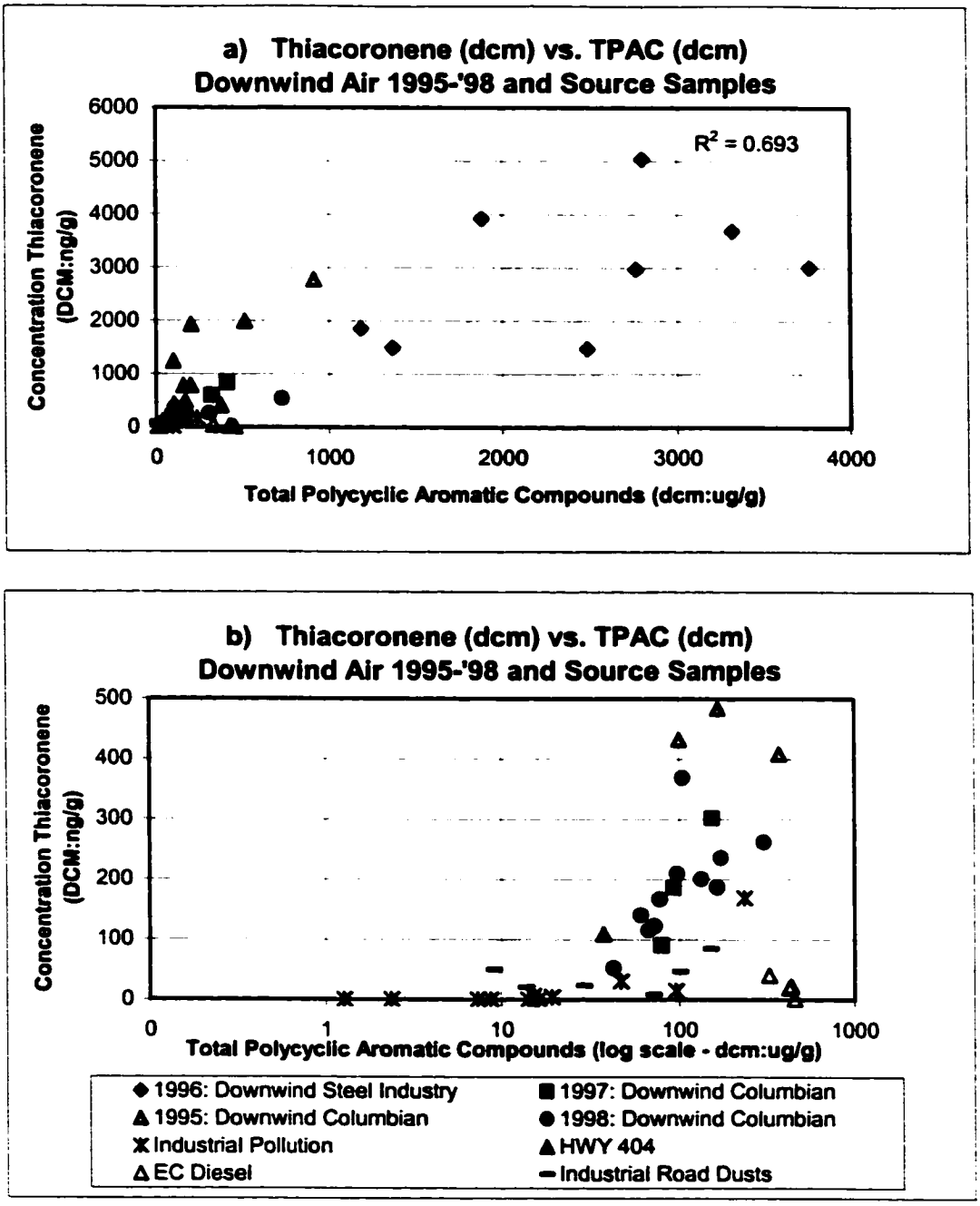


Figure 5.5. Relationship between concentration of thiacoronene in the dichloromethane extract and the total concentration of PAC for air samples collected downwind of the steel industry, downwind of a carbon black plant and source samples. Chart b) is an expansion of the lower left region of Chart a) with the x axis on a log scale.

5.5.1.2. Thiacoronene Extracted by Toluene vs. Total Polycyclic Aromatic Compounds (TPAC)

In Figure 5.6 (a), the thiacoronene (toluene) level is plotted against the dichloromethane TPAC value for the source samples. We do not see the linear trend that was seen for thiacoronene (DCM) vs. TPAC. The air particulate containing coke oven emissions (represented by diamonds) exhibit TPAC values as high as 3760 μg/g and thiacoronene (toluene) levels lower than 24 ng/g (data in Table 5.2). These thiacoronene levels in the toluene extracts of the coke oven-impacted air samples are extremely low compared to those found in the dichloromethane extracts, which were up to 5000 ng/g. Figure 5.6 (b) is the same plot, but is an expansion of the low thiacoronene region in the bottom left corner to provide a better view of the source sample data points. This Figure also has the industrial pollution samples broken down into specific sample types including coals, coal breeze, Environment Canada diesel particulate (EC Diesel), coking-related samples, blast furnace dusts and industrial road dusts. Coking-related samples (DOPEM) and vehicular emissions from highway 404, and coal breeze exhibit relatively low TPAC values and thiacoronene levels (toluene) on the order of those seen for coke oven emissions. Steel industry blast furnace dusts and industrial road dusts both exhibit low levels of thiacoronene and TPAC. Coals have extremely low levels of TPAC (7-16 μg/g), contrary to Environment Canada diesel particulate samples (320 - 450 μg/g), but both contain levels of thiacoronene below detection limit (0.3 to 1.3 ng/g) in the toluene extracts.

This data can also be viewed using a logarithmic scale for the TPAC axis as seen in Figure 5.7 to show the enormous range of TPAC values for the source samples. The source samples including EC diesel, coal breeze, coals, blast furnace dusts and road dusts have been grouped together in this plot. This figure shows that the thiacoronene (toluene) levels in all source samples (shown as stars) are negligible compared to air samples collected downwind of the carbon black plant (up to 640 ng/g; 1995 - triangles, 1997 - squares, 1998 - circles). For source samples related to coke oven and other steel industry emissions, the thiacoronene levels did not exceed 31 ng/g even though the TPAC values ranged over 5 orders of magnitude (range 0.03 to 3760 μg/g).

The figures in this section demonstrate that industrial pollution emissions do not appear to have significant thiacoronene contents, and whatever thiacoronene they do contain is efficiently extracted out in the initial dichloromethane extraction. Therefore, steel industry emissions, vehicular emissions, diesel emissions and road dusts do not pose significant interferences in the carbon black method. On the other hand, for the samples that were classified as downwind of the carbon black plant in 1995, 1997, and 1998, the thiacoronene levels (toluene) ranged between 10 and 641 ng/g (Table 5.2). Many of these samples exhibited higher thiacoronene levels (toluene) than source samples and are considered to have significant carbon black impacts.

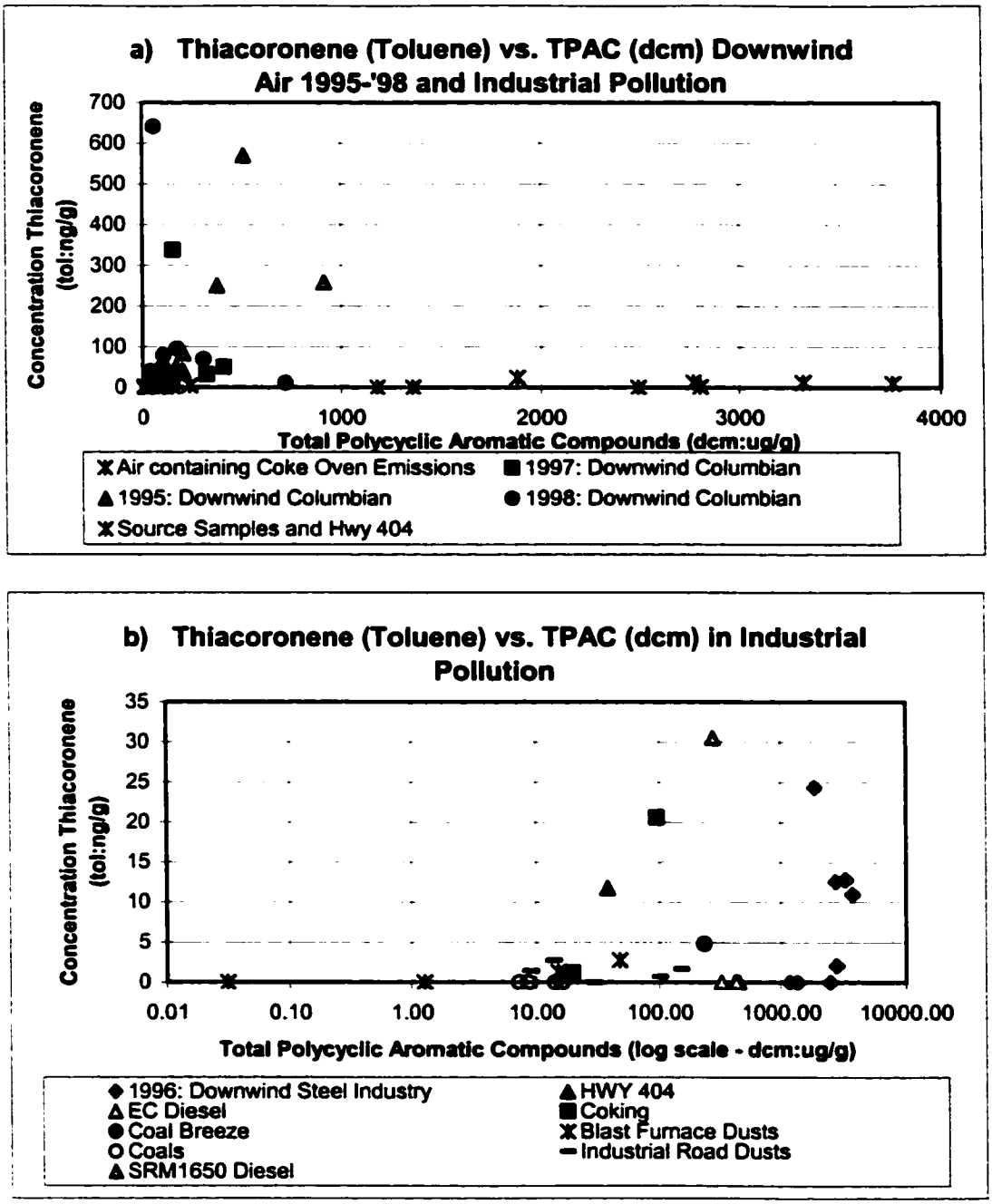


Figure 5.6. Relationship between concentration of thiacoronene in the toluene extract and the total concentration of PAC for air samples collected downwind of the steel industry, downwind of a carbon black plant and for source samples. Chart b) is an expansion of the lower left region of chart a) with the x axis on a log scale.

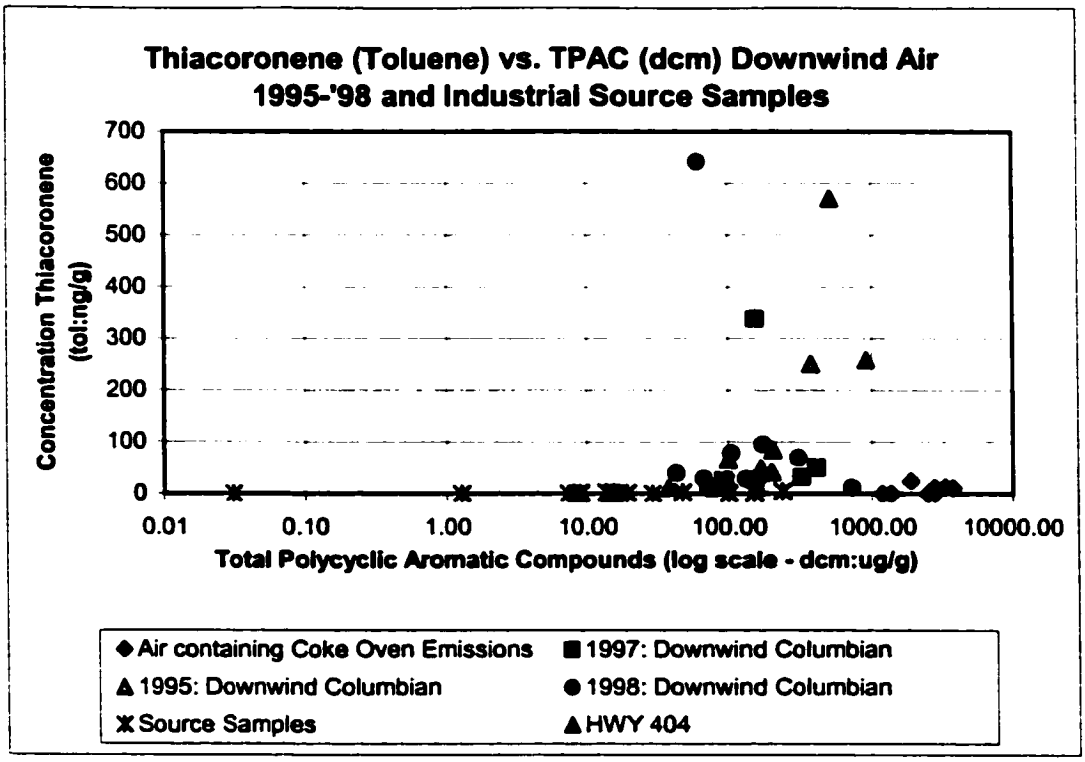


Figure 5.7. Relationship between concentration of thiacoronene in the toluene extract and the total concentration of PAC (log scale) for air samples collected downwind of a carbon black plant, downwind of the steel industry and for source samples.

5.5.2. *Determination of a "Carbon Black Threshold"*

Using our carbon black monitoring data spanning four years, and the pollution source data described herein, we have established a "carbon black threshold" as a way of defining carbon black impacts in air particulate. The carbon black threshold would be represented by a thiacoronene level (toluene extract), above which air samples would be positively identified as having significant carbon black impacts, and below which impacts from carbon black could not be positively identified. This is achieved using the type of Figure which plots thiacoronene (toluene) versus TPAC (DCM).

Only the thiacoronene data from pollution sources were considered in the generation of the carbon black threshold (including the steel industry source samples, the air samples containing coke oven emissions, the HWY 404 vehicular emission samples, the EC diesel particulate emission samples and the diesel reference material SRM 1650). The pollution source data are represented in a plot of of thiacoronene level (in toluene) versus total polycyclic aromatic compounds (in dichloromethane) in Figure 5.8 (a). A simple regression analysis was performed to calculate a straight line that best fits this data using the "least squares" method. The calculated line of best fit in the form of $Y = mx + b$ was $Y = 0.0020x + 3.11$ and is shown as a dotted line with data points as closed circles in Figure 5.8 (b). The 95% confidence interval for the mean value of Y (thiacoronene in toluene) was calculated for each value of X (TPAC) and is expressed as error bars in the Y dimension on the line of best fit. This 95% confidence interval[158] included the range in which we can be 95% confident that the mean lies for thiacoronene (toluene) levels of source samples other than

carbon black. A prediction interval for Y at two levels of confidence was also calculated. A 95% prediction interval (shown as stars on Figure 5.8 (b)) and a 98% prediction interval (shown as X's on the same Figure) for Y (thiacoronene in toluene) was calculated for each value of X (TPAC). These prediction intervals[158] define lines below which we are 95% or 98% confident that the thiacoronene (toluene) levels for pollution sources other than carbon black will lie.

A more conservative statistical measure, the 98% prediction interval, statistically predicts that samples containing pollution sources other than carbon black will have thiacoronene (toluene) levels below the 98% prediction interval for a certain value of X or TPAC (based on our pollution source data). This 98% prediction interval data (ranging from 21 to 30 ng/g thiacoronene in the toluene extract with an average of 23 ng/g) was used to create the carbon black threshold. The 98% prediction interval line is shown in Figure 5.9 as a polynomial linear trend line which was drawn to best fit the prediction interval data using the equation $Y = 2E\text{-}07x^2 + 0.0017x + 21.27$ and the value of x, or TPAC level from the pollution source data. The Y intercept of the line is approximately 21 ng/g thiacoronene in the toluene extract. As a result of this statistical analysis, we propose the use of this line created by the 98% prediction interval to be used as a "carbon black threshold" for the determination of carbon black impacts in air particulate. The carbon black threshold may be approximated as 23 ng thiacoronene per gram of particulate (the average value calculated by the 98% prediction interval) or 1.5 mg carbon black per gram of particulate. This carbon

black threshold would facilitate the identification of air particulate samples containing carbon black impacts.

In order to use this threshold, air samples would be plotted graphically in the TPAC (dcm: μg/g) versus thiacoronene (toluene: ng/g) figure bearing the carbon black threshold. Data points lying above the carbon black threshold would be classified as having positive carbon black impacts, and data points on or below the carbon black threshold would be classified as having insignificant or no carbon black impacts. Examples of graphs exhibiting the carbon black threshold are shown in Figure 5.9 and Figure 5.10. Figure 5.9 illustrates the X axis, or the TPAC data on a logarithmic scale, and Figure 5.10 has both axes on a logarithmic scale in order to make the low and high data points more clearly visible.

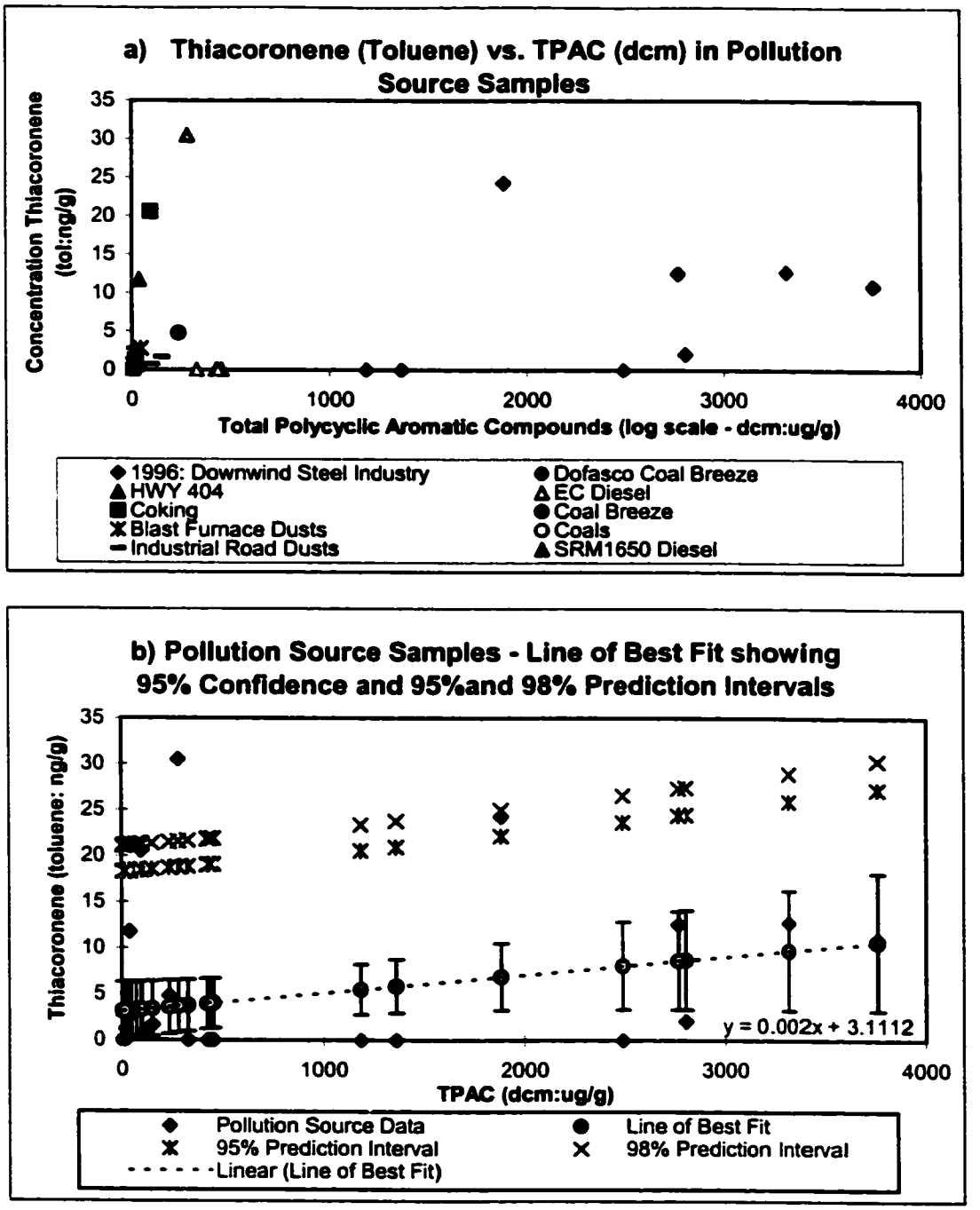


Figure 5.8. a) Relationship between concentration of thiacoronene in the toluene extract and the total concentration of PAC for air collected downwind of the steel industry and for source samples. b) Development of a carbon black threshold for the same data using a 95% confidence interval and 95 and 98% prediction intervals.

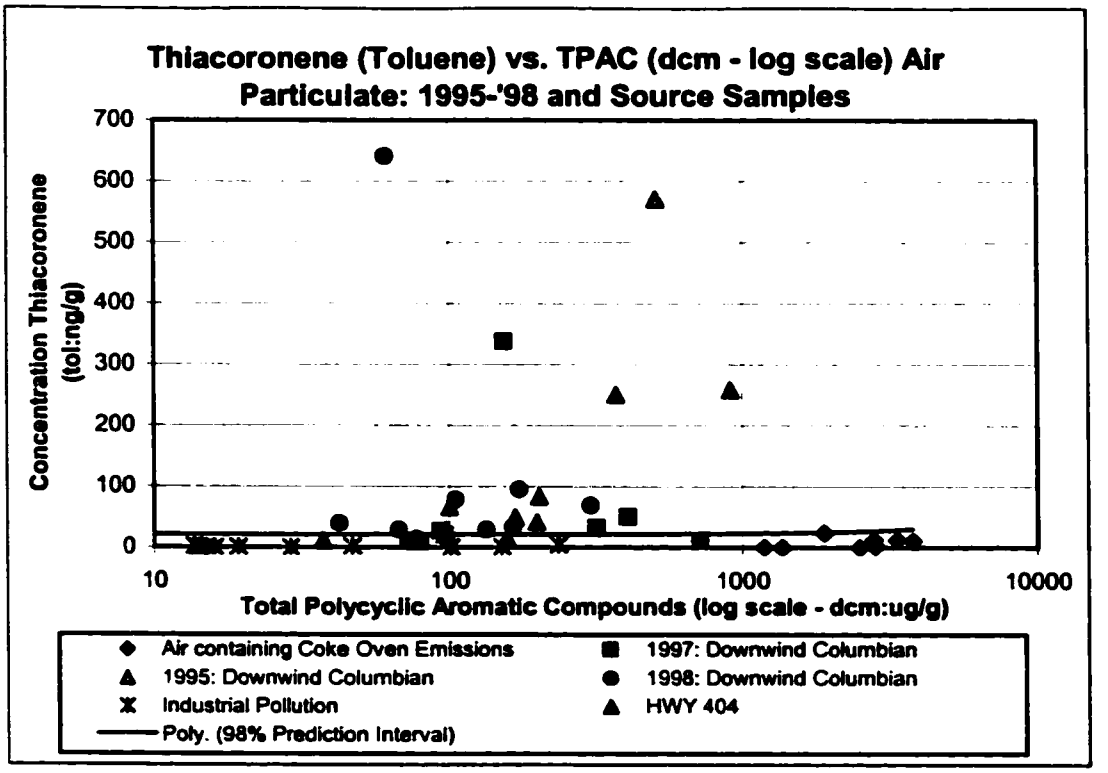


Figure 5.9. Relationship between concentration of thiacoronene in the toluene extract and the total concentration of PAC (log scale) for air samples collected downwind of a carbon black plant, downwind of the steel industry and for source samples. The horizontal line indicates the 98% prediction interval, below which air samples containing pollution sources other than carbon black will lie.

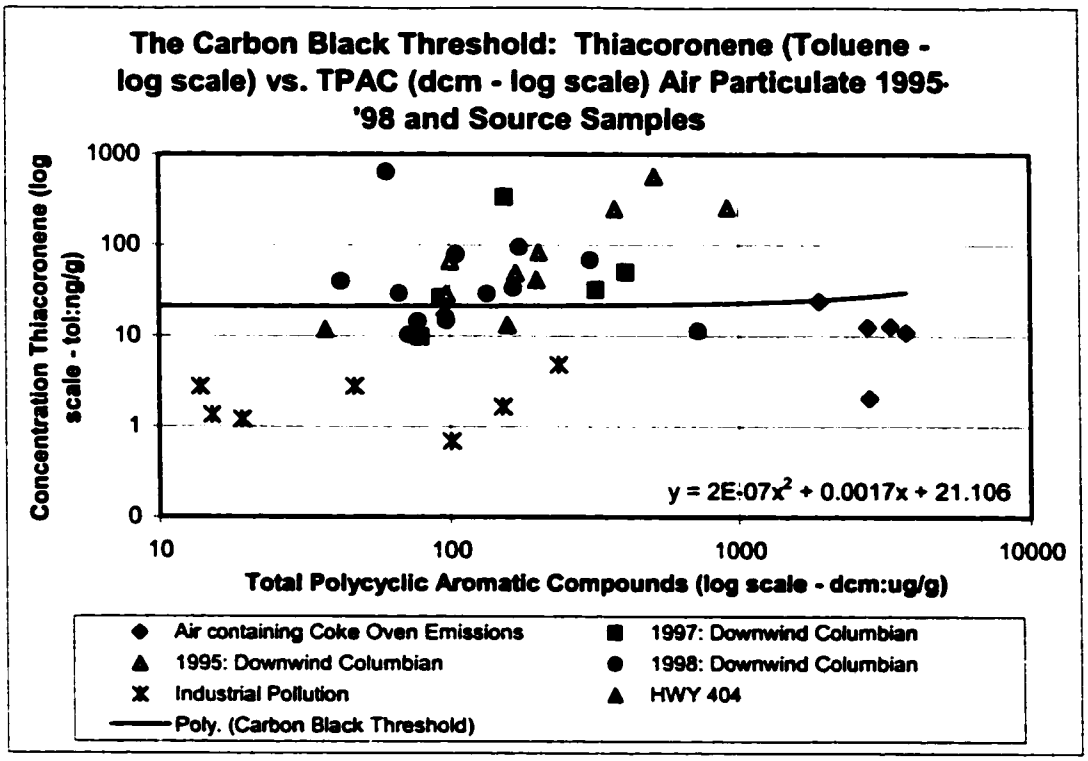


Figure 5.10. Relationship between concentration of thiacoronene in the toluene extract (log scale) and the total concentration of PAC (log scale) for air samples collected downwind of a carbon black plant, downwind of the steel industry and for source samples. The horizontal line indicates the "Carbon Black Threshold" (or 98% prediction interval), below which air samples containing pollution sources other than carbon black will lie.

5.6. APPLICATION OF THE CARBON BLACK THRESHOLD

In our air monitoring campaign spanning 4 years, we identified 24 sampling dates as having the greatest potential for carbon black impacts. On those sampling dates, air particulate was collected upwind and downwind of the carbon black plant simultaneously. If there were releases of carbon black from the plant, whether from accidental releases or from fugitive emissions, we would expect to see evidence of these releases in our downwind air samples. Using the carbon black threshold, we can see in Figure 5.11 how our air particulate samples become classified. Of the twenty-four air particulate samples collected downwind of the plant, eighteen were found to have thiacoronene values above the threshold and thus has measurable carbon black impacts (solid data points above the carbon black threshold - Figure 5.11). Six of the downwind samples lie below the carbon black threshold, indicating insignificant or no carbon black impacts (open data points below the carbon black threshold). Overall, three-quarters of the air samples collected downwind of the carbon black plant had values above the carbon black threshold and thus resulted in carbon black impacts. Of the samples collected upwind of the carbon black plant, the average thiacoronene concentration associated with background air particulate (0.12 ± 0.11 pg/m^3 or 4.9 ± 4.3 ng/g, see Section 4.6.1) corresponds to a carbon black concentration of 0.33 mg/g.

Figure 5.12 illustrates the classification of carbon black impacts according to the concentration of carbon black detected downwind in units of mg/g (Figure 5.12 a), and in units of $\mu g/m^3$ (Figure 5.12 b). The upper chart contains a line representing the

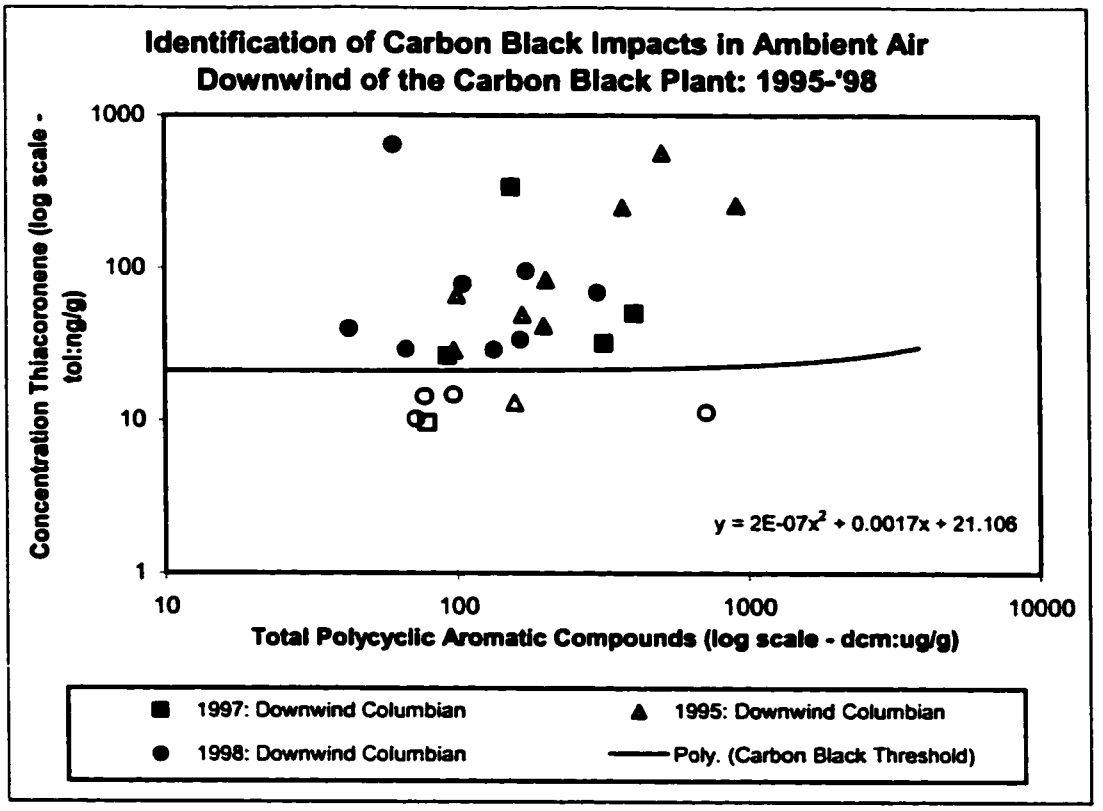


Figure 5.11 Identification of carbon black impacts downwind of the carbon black plant in air samples collected in the 1995, 1997 and 1998 air monitoring campaigns. The horizontal line indicates the "Carbon Black Threshold" below which air samples containing pollution sources other than carbon black will lie (open data points).

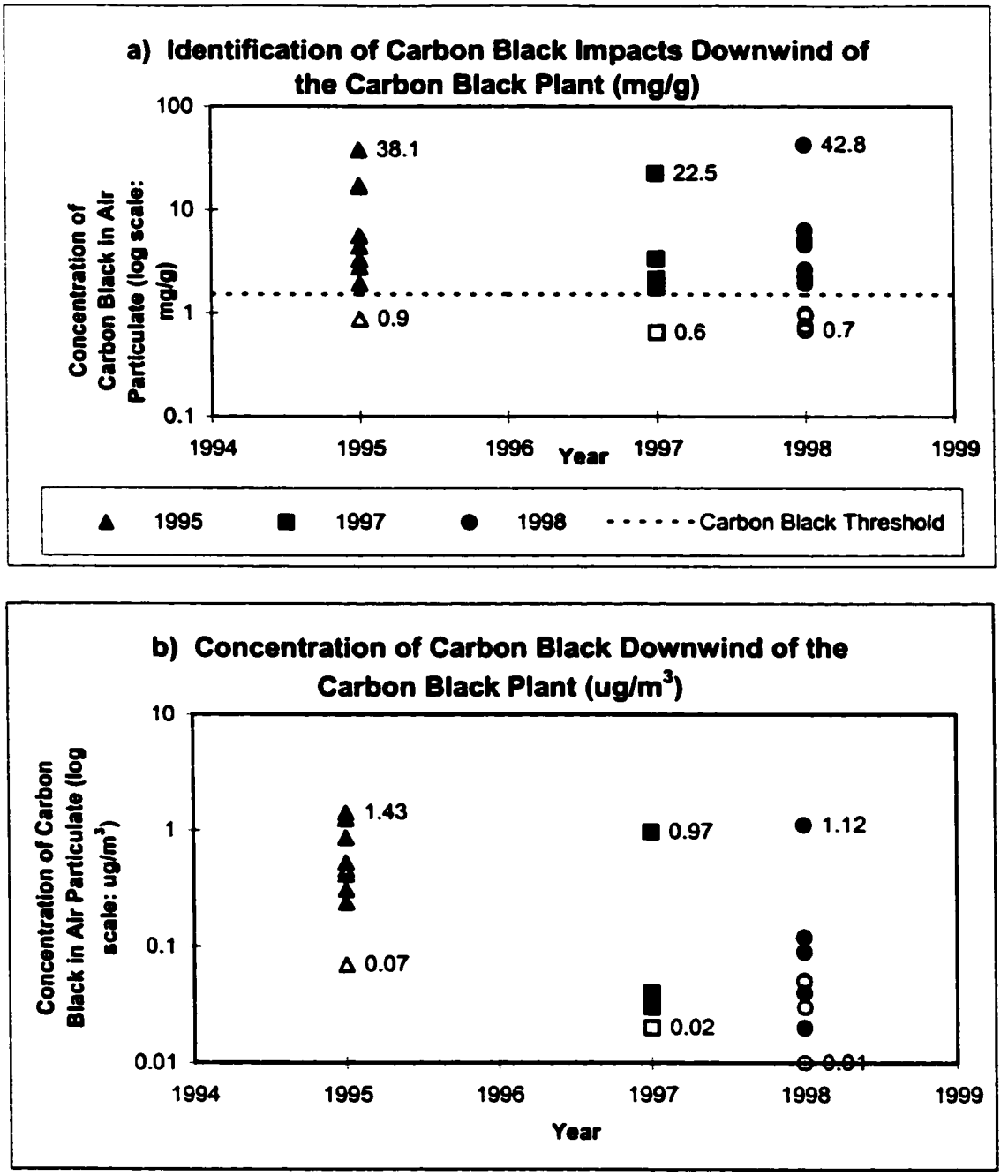


Figure 5.12: Identification of carbon black impacts downwind of a carbon black plant in a) mg carbon black per gram air particulate, b) mg carbon black per meter cubed of air (closed data points denote carbon black impacts as identified by the carbon black threshold).

approximated carbon black threshold (1.5 mg carbon black per gram particulate). The lower chart is a representation similar to one at the end of Chapter 4 (Figure 4.2) in units of μg carbon black per m^3 of air; the samples classified by the threshold as having carbon black impacts are depicted using solid data points and the samples with no impacts are depicted with open data points. The lower chart shows that the samples having the lowest calculated concentration of carbon black in $\mu g/m^3$ are not always the samples having the lowest carbon black impacts in mg/g. Air samples may or may not have heavy particulate loadings depending on the amount of particulate in the air during the sampling period. Therefore, samples having the same carbon black impact in $\mu g/m^3$ may have very different impacts in terms of mg/g depending on the amount of particulate collected. Since the carbon black threshold is based on thiacoronene levels in source samples (on a mass/mass basis), the threshold is limited to classification of air samples on a mass/mass basis.

The significance of the carbon black impacts calculated for the residential dust samples of black fallout described in Section 4.5 can be evaluated using the carbon black threshold. The maximum carbon black impacts in these dust samples was calculated assuming that all of the thiacoronene detected in the samples was derived from carbon black. The three residential dust samples in Table 4.4 had calculated carbon black impacts ranging from 0.80 to 1.7 mg/g. The floating dust samples taken from Lake Ontario had calculated carbon black impacts ranging from 3.4 to 9.6 mg/g. Of these dust samples, one of the three residential dusts and all of the floating dusts from lake Ontario had carbon black concentrations above the carbon black threshold (1.5 mg/g) indicating significant carbon

black impacts in those samples. The remainder of the dust samples had calculated carbon black impacts below the carbon black threshold (0.80 and 1.2 mg/g) which were still higher than average background air particulate collected upwind of the carbon black plant (0.33 mg/g).

5.7. CHAPTER SUMMARY

We have evaluated the relationship between thiacoronene levels in the extracts and the total PAC levels of source samples other than carbon black. Knowing this relationship, we were able to assess the potential interferences of these source samples in carbon black determinations. Our findings showed that using our sequential extraction method, the levels of thiacoronene in the toluene extracts of industrial source samples are negligible in comparison to levels in carbon blacks. In those source samples that contain thiacoronene, the majority of thiacoronene (>90%) is extracted by dichloromethane. From these evaluations, we concluded that thiacoronene is a useful marker for carbon black in ambient air particulate.

Our source samples also served in the development of a carbon black threshold. This threshold was useful as a tool in the identification of carbon black impacts in ambient air particulate and in black fallout dust samples. As this source apportionment research continues and other potential source samples become available for analysis, these data will be added to the database and the statistical analysis yielding the carbon black threshold will be redetermined. With the collection and analysis of more air particulate samples and source samples in years to come, the carbon black threshold may change and perhaps become lower as the statistical sample size increases.

6. INORGANIC ELEMENTS AND POLYCYCLIC AROMATIC COMPOUNDS AS SOURCE APPORTIONMENT TRACERS IN URBAN AIR

6.1. INTRODUCTION

Results from a recent chemical source apportionment study conducted by Harrison *et al.* demonstrated that a combination of PAH and inorganic pollutant measurements is a more powerful tracer of emission sources than PAH data alone.[27] The use of polycyclic aromatic compounds and thia-arenes as source tracers has been explored in our research group. Using thia-arene (PASH) profiles, L.M. Allan was able to distinguish between petrogenic emissions and coke oven emissions in air particulate collected in Hamilton, Ontario.[144] The research described herein has identified a new thia-arene source tracer, thiacoronene, for the quantitation of carbon black in ambient air particulate. One of the goals of this thesis was to investigate inorganic source apportionment strategies that could be used in parallel with, or, as a potential replacement for organic source apportionment methods. We foresaw an opportunity to compare the organic and inorganic methodologies directly using the samples discussed in this thesis.

In this chapter, we will report data from ambient samples for elements that are characteristic of potential pollutants from metallurgical processes, coking, coal and petrogenic fuel combustion emissions. Metal levels in ambient air particulate sampled upwind and downwind of the steel mills were obtained from ICP-MS analyses of acid

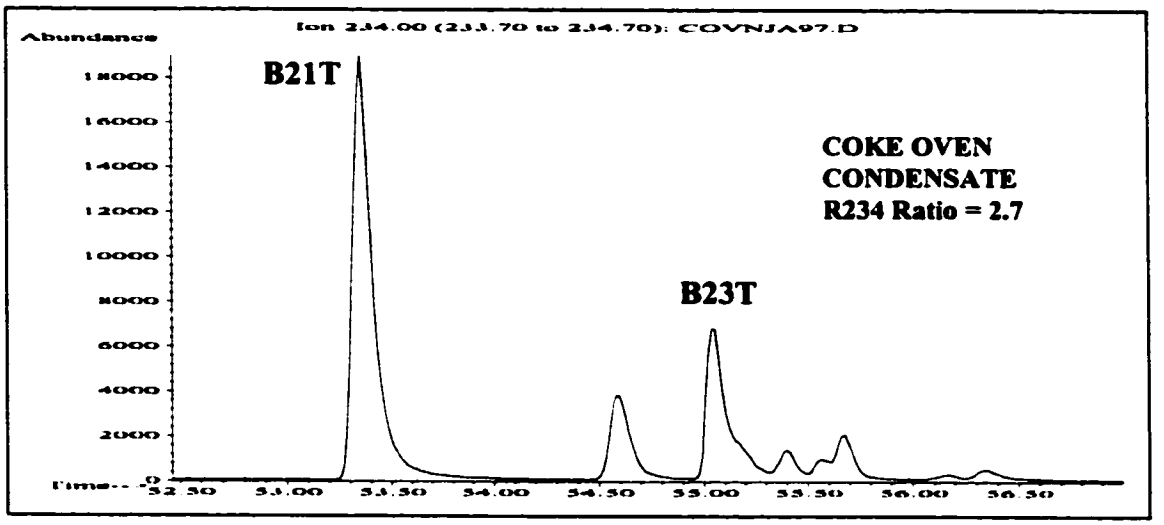
digests of filter samples. These data were compared in efforts to identify impacts from the metallurgical industry in ambient air samples.

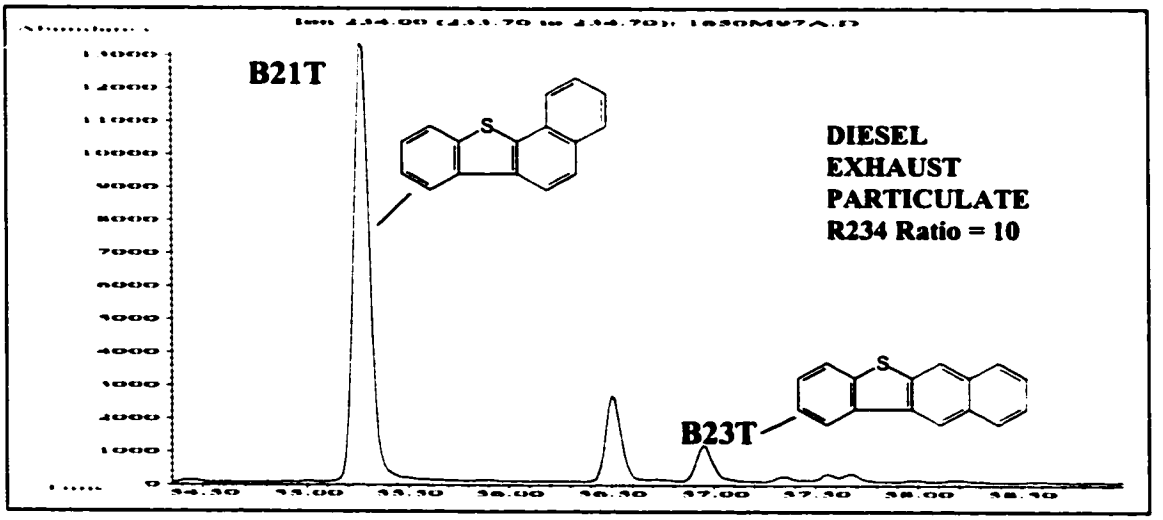
6.1.1. Source Apportionment of Steel Industry Coke Oven and Petrogenic Emissions Using Thia-arenes: 1995 Study

Dr. L.M. Allan's Ph.D. thesis dealt with the development of a source apportionment method based on the analysis of thia-arenes, specifically those with masses of 234 and 258 Da. Ratios of specific 234 and 258 Da PASH isomers were shown to be suitable source tracers for distinguishing coke oven emissions from petrogenic fuel combustion emissions in Hamilton air particulate samples. The 234 and 258 Da thia-arenes are relatively non-volatile and are well-suited for particulate analysis. This source apportionment method was based on the difference between the 234 Da profile observed for coke oven condensate and a reference diesel exhaust particulate (SRM 1650, see Figure 6.1). The ratios of the peak areas of two 234 Da thia-arene peaks were found to be quite different in these samples. Similarly, the peak area ratios of certain 258 Da thia-arenes were also found to be useful source tracers and an R258 ratio was also developed. In the present research, the levels of the 258 Da thia-arene isomers were generally below the detection limit in many of the samples analysed and thus were not used.

The ratio of the peaks labelled B21T (benzo[b]naphtho[2,1-d]thiophene) and B23T (benzo[b]naphtho[2,3-d]thiophene) in Figure 6.1 was found to be the most useful source indicator after principal component analyses. For the B23T peak, if more than one isomer was found co-eluting, the entire area under the peak is quantified for the ratio.

Figure 6.1: Mass Chromatograms of the m/z 234 ion from the analyses of coke oven condensate (top) and diesel exhaust particulate (bottom). The ratio of peaks B21T and B23T were used as the source apportionment criterion.





The thia-arene ratio (R234) was defined as the ratio of two peak areas:

$$R234 = \frac{\text{Peak Area B21T}}{\text{Peak Area B23T}}$$

The R234 ratio was found to be 10 for diesel exhaust particulate (SRM 1650) and 2.7 for coke oven condensate and coal tar (SRM 1597).

Allan used air particulate samples collected in 1995 to evaluate the efficacy of the 234 Da thia-arenes as source apportionment tracers.[144] Samples were collected at five locations, two of which were upwind and downwind of the steel industry coke oven batteries; other locations were in high traffic areas where diesel impacts were expected to be significant. The total PAH levels for samples collected upwind of the coke ovens ranged from 0.17 to 2.1 ng/m^3, while for the downwind samples the values ranged from 17 to 150 ng/m^3. Thus, the values range over 3 orders of magnitude (from 0.17 to 150 ng/m^3), corresponding to a very broad range of air particulate pollution. The 234 Da thia-arene profiles for air particulate samples collected downwind of the coke ovens were found to be similar to the thia-arene profiles for coke oven condensate and coal tar (SRM 1597). The thia-arene profile for the upwind air samples more closely resembled that of diesel exhaust particulate (SRM 1650). The air samples collected in the 1995 air monitoring campaign were designated as having coke oven-like character or petrogenic fuel emission-like character by using the following convention: samples having a 234 Da ratio greater than or equal to 3.1 were designated as having petrogenic character, while samples having a 234 Da ratio less than 3.1 were designated as having coke oven

emissions character.

The relationship between the R234 thia-arene ratio and total PAH for all of the 1995 Hamilton air samples is illustrated in Figure 6.2. In this figure, the 234 Da thia-arene ratio of each air sample is plotted against total PAH concentration (upper plot) and against the log of the total PAH concentration (lower plot). A non-linear relationship is observed in both plots. The R234 ratio decreases rapidly with increasing PAH concentration to about 5 ng/m^3. Above 5 ng/m^3 there is no apparent change in the ratio, indicating a dominance of coke oven emissions. The horizontal dashed line represents the value of the 234 Da thia-arene ratio of 3.1, below which air samples are classified as having coke oven character, and above which air samples are classified as having petrogenic character. In the lower plot of Figure 6.2 the vertical dashed lines bracket those 1995 ambient air samples that had mixed source contributions. Some of the samples within the total PAH range bracketed by these vertical lines had coke oven designations, while others had petrogenic designations, therefore, this region was found to have mixed source contributions.

6.2. APPLICATION OF THE THIA-ARENE RATIO APPROACH

A study to monitor air particulate downwind of the steel industry's coke ovens was undertaken in 1996.[153] All samples were collected at the Pier 25 site, an MOE air sampling site located 1.5 km east of the coke ovens of the nearest steel mill and is usually downwind of the steel mills during the prevailing winds from the west. Compared to the 1995 samples, the majority of the 1996 samples were heavily impacted by coke ovens. In

April and May of 1996, 24-hour PM10 samples were collected over a 51 day period; of these, 35 were selected for extraction with dichloromethane and were analysed for PAH by L. Heydorn as part of her undergraduate thesis. Ten of these samples were then extracted with toluene and were analysed by this author as described previously (Chapter 5). The impacts of the steel industry coke ovens in these samples were determined by PAH and thia-arene analyses performed by L. Heydorn.[153] Indeed, it was difficult to find samples with low level impacts at this site because of its proximity to the coke ovens, and the fact that the coke ovens operate continuously. Even when the wind was blowing from a direction such that the sampler was upwind of the coke ovens for most of the day, the total PAC levels indicated that there had to have been modest impacts of coke oven emissions at the sampler. These impacts were due to winds blowing from the coke ovens for short periods, to periods of very slow wind velocities, or to re-entrainment of coke oven-contaminated road dusts. We are not confident that any true upwind (zero industrial impact) samples were collected in 1996 due to the proximity to the coke ovens. Therefore, in our evaluation, air samples collected in 1997 and 1998 at the pool site (see Map 5.1) having low TPAC values (< 1.5 ng/m^3) were used to represent low-to-minimal impacts from the steel industry.

The pool site was an ideal upwind sampling location, as it was more than 2 km from the steel industry and only 100 m from the shore of Lake Ontario. Wind coming off Lake Ontario carried with it no locally-generated pollutants. Ten upwind samples from the Pool site in 1997 and 1998 and three upwind samples from Pier 25 in 1996 were used in these assessments. The potential for impacts from steel industry activities and from

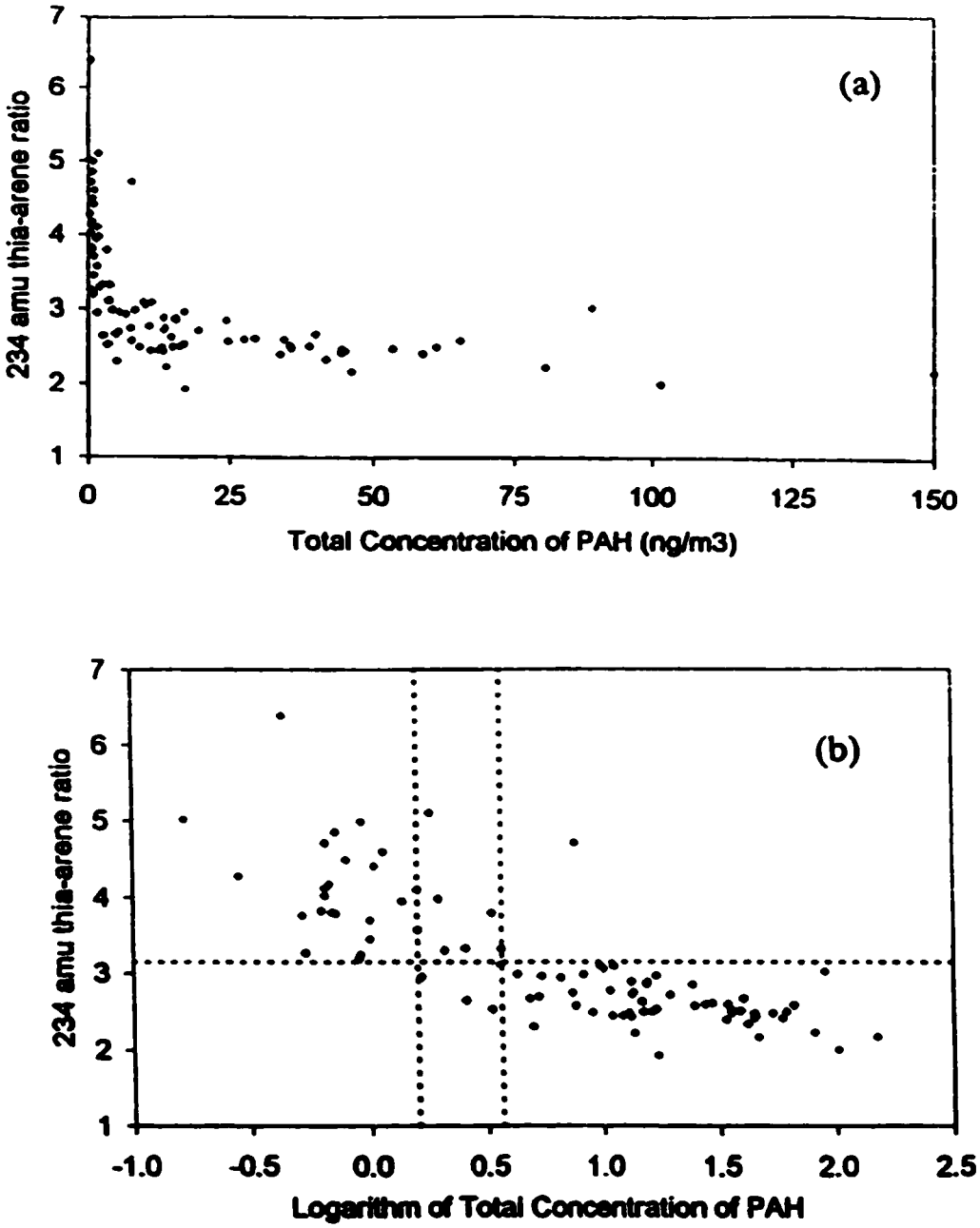
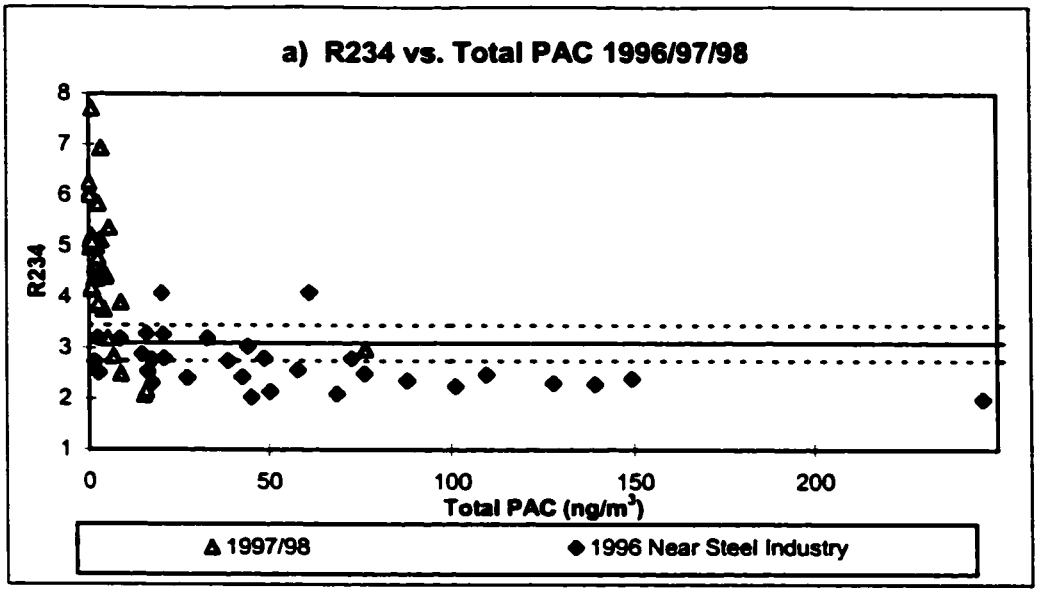


Figure 6.2: Relationship between 234 Da ratio and a) total concentration of PAH and b) the logarithm of the total concentration of PAH for 89 Hamilton air particulate samples. The horizontal dashed line has an R234 = 3.1. Vertical dashed lines bracket samples with mixed source contributions. (Figure taken from L.M. Allan's Ph.D. thesis - Figure 7.5, reference 118).



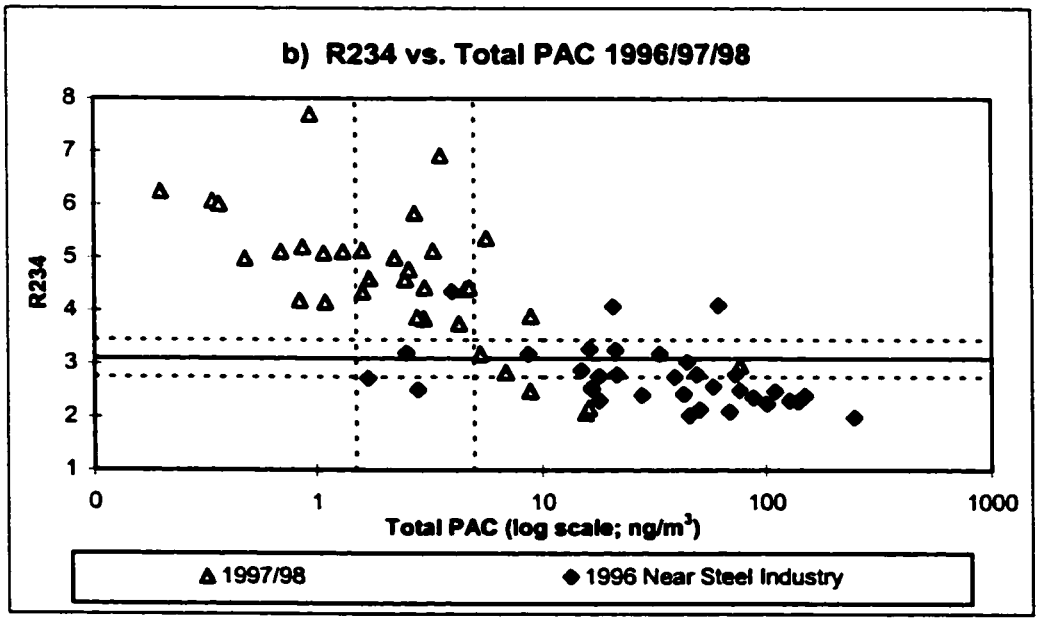


Figure 6.3. Relationship between the 234 Da thia-arene ratio and (a) total concentration of PAC on a linear scale and (b) total concentration of PAC (log scale) for all air samples collected in 1996 - 1998. The vertical lines represent the TPAC = 1.5 - 5 ng/m^3 and the horizontal lines, an R234 = 3.1 +/- 0.35.

blowing dusts and fugitive emissions which had collected on the ground around the Pier 25 site were kept in consideration for the latter three samples from Pier 25.

Plots of the 234 Da thia-arene ratio vs. TPAC similar to Figure 6.2 (1995 data) for all of the air samples studied in this thesis in 1996, 1997 and 1998 data are shown in Figure 6.3. In the 1996 data set, there are no samples with R234 ratios above a value of 4.5. This indicates that many of the 1996 samples were impacted by coke oven emissions. The 1997/1998 data set contains 11 samples having R234 ratios indicative of diesel/petrogenic emissions (see upper left quadrant of Figure 6.3 b). Three of the 1997/1998 samples lie in the lower right quadrant (Figure 6.3 b) with R234 ratios indicative of coke oven impacts. The remaining 18 samples from those years appear to have mixed source contributions. All of the samples within the region bracketed by the two vertical lines are indicative of mixed source contributions.

6.3. THE EVALUATION OF A NEW SOURCE APPORTIONMENT STRATEGY USING METALS AND PAC

With the success of a source apportionment method based on the ratios of thia-arene isomers, we wondered about the potential to incorporate inorganic elements in a source apportionment scheme. We felt that an evaluation of the metals known to be released by steel manufacturing and coking emissions would be a good starting point.

Our carbon black source apportionment study showed that the majority of the "black fallout" in the east-end of Hamilton was derived from pollution sources other than carbon black. This conclusion was based on the analysis of residential dust samples of

black fallout and ambient air particulate collected downwind of the carbon black plant. Potential sources of black particulate (other than carbon black) include steel industry derived particulates from coking ovens, blast furnaces, rolling mills and fugitive emissions from outdoor coal, coke and slag piles and road dusts. There could also be potential contributions from vehicular emissions and smaller industries. Our objective was to develop a new source apportionment strategy for steel industry-derived air particulate using metals and polycyclic aromatic compounds data hand in hand. We also wanted to compare the use of metal source tracers versus organic (PAC) source tracers for the source apportionment of steel industry emissions.

The potential advantages of looking at metal source tracers versus PAC source tracers include lower analytical costs, faster sample turnaround times and the fact that metals analysis could potentially be used as a rapid screening tool to assess samples for specific industrial impacts. In terms of cost, the laboratory cost for PAC analysis is on the order of $200/sample whereas each ICP-MS analysis costs approximately $25/sample for a full suite of metals.

Sample preparation times for analysis are greater for PAC analysis, as the preparations are more rigorous. Sample preparation for ICP-MS analysis is quite simple and rapid, including sieving (if required) or cutting of the air filters (25 mm diameter disks) and addition of solution for digestion (HNO_3/H_2O_2). The sample turnaround times for metals analysis by ICP-MS is on the order of a couple of days, whereas the PAC analysis would take the better part of a week or more depending if a second extraction is

involved (producing two extracts per sample). The metals analysis by ICP-MS could potentially be used as a rapid screening tool for industrial impacts prior to organic analysis, thereby reducing the number of samples targeted for the more time-consuming and costly PAC analysis.

6.3.1. *Metals Associated with Steel Industry Processes*

Winchester and Nifong evaluated whether air pollution along the southwestern shore of Lake Michigan could be a significant source of trace element contamination in Lake Michigan.[28] Data were tabulated for the estimated amount of emissions per year for 30 trace elements from coal burning sources, coke manufacture, fuel oil combustion, iron and steel manufacture, cement manufacture and transportation sources. The trace elements most commonly emitted from iron and steel operations in the literature were Fe, Mn, Cu, and Zn, whereas coal, coke and fuel oil combustion were mainly responsible for As, Cr, Sn, Ti, Ni, and V emissions.[28,154-156]

A major source of local metals release data for steel manufacturing comes from Dofasco Inc. In 1997, Dofasco took a proactive step by signing an Environmental Management Agreement (EMA) with Environment Canada and Ontario's Ministry of the Environment. The agreement includes specific objectives for pollution reductions. One of these reports is the National Pollutant Release Inventory Report (NPRI) to Environment Canada, released yearly since 1997.[159] Some of the data for the years relevant to this research is tabulated in Table 6.1.

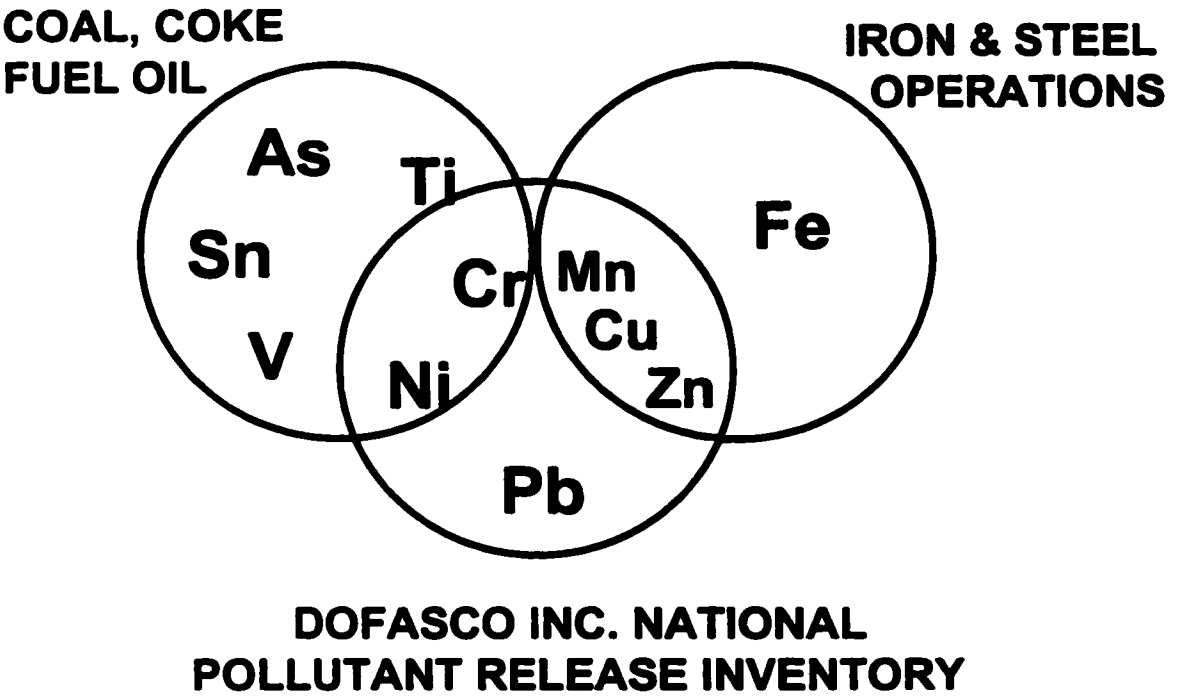
The levels of metals released to the air and water by Dofasco between 1996 and 1998 ranged from 0.004 tonnes per year (Ni) to 18.6 (Zn) tonnes per year. According to the NPRI reports, the majority of the metal releases originate from the electric arc furnace (EAF) baghouse and from fumes from the basic oxygen furnace (BOF). The PAC releases reported were for the low molecular weight PAC, naphthalene and anthracene. These PAC releases, on the order of 0.6 to 11.4 tonnes per year to the air were related to emission controls at the coke plant by-product areas and also related to leaks in the coke battery.

Figure 6.4 shows the metal releases associated with iron and steel operations (upper right circle) and coal, coke and fuel oil contributions (upper left circle). The metals reported in the Dofasco NPRI report are also shown (lower middle circle). It is curious that iron was not one of the metals reported by Dofasco, as one would expect that iron would be released in great quantities from an iron and steel manufacturer. We decided to focus our first inorganic source apportionment study on the metals displayed in Figure 6.4 as they are directly associated with steel industry processes in the literature and in the Dofasco NPRI reports.[116,159]

Table 6.1: An excerpt from the National Pollutant Release Inventory Report for Dofasco Inc.

Substance Name	Direct Release to the Environment (Tonnes/year)			Primary Releases		
	1996	1997	1998	Air	Water	Action Plan to Reduce Emissions
Anthracene	0.64	0.63	0.60	◆		Coke Battery leak reduction program
Benzene	456	314	290	◆		Emission controls at Coke Plant By-product areas
Naphthalene	11.4	9.4	9.2	◆		Emission controls at Coke Plant By-product areas and Coke Battery leak reduction program
Chromium and its compounds	0.18	0.30	0.24	◆	◆	Primary recirculation system; EAF baghouse upgrade; BOF fume collection system improvement plan
Copper and its compounds	0.02	0.16	0.15	◆		EAF baghouse upgrade; BOF fume collection system improvement plan
Lead and its compounds	0.58	0.94	0.62	◆	◆	Primary recirculation system; EAF baghouse upgrade; BOF fume collection system improvement plan
Manganese and its compounds	5.4	6.7	3.8	◆	◆	Primary recirculation system; EAF baghouse upgrade; BOF fume collection system improvement plan
Nickel and its compounds	0.004	0.09	0.09	◆		EAF baghouse upgrade; BOF fume collection system improvement plan
Zinc and its compounds	11	18.6	16.4	◆	◆	Primary recirculation system; EAF baghouse upgrade; BOF fume collection system improvement plan

Figure 6.4: Metals released by sources including: coal, coke, fuel oil combustion, iron and steel operations. Metals documented as releases by Dofasco Inc. in the NPRI reports (1996-1998).



6.3.2. *Inorganic Analyses*

In this study we examined the metals associated with PM_{10} collected upwind and downwind of the steel industry. The air samples were analysed for their metal contents by cutting a 25 mm diameter circle from each filter prior to extraction using a cutting stamp and sending these sections to Activation Labs (Ancaster, ON) for dissolution and ICP-MS analysis. Blank filters were also examined. The concentrations of the 11 metals in the ambient air samples are listed in Appendix VIII. Air samples from 1995 were not selected for inorganic analysis, as they had been previously extracted and we didn't know whether the metals data from these extracted filters would be meaningful.

6.3.2.1. *Effect of Organic Extraction on Metals Levels in Air Particulate Samples*

We wanted to assess whether prior organic extractions (Soxhlet) of filters had any impact on the quality of the metals data before proceeding with ICP-MS analyses of any of the 1995 samples. A selection of 10 air particulate samples (filter #1491-1500) from the 1996 air monitoring campaign were chosen for this study.

A portion of each air filter was cut for ICP-MS analysis (as described previously) prior to organic extraction and then a second portion was cut following the organic extraction. The filter portions were cut from similar locations on the air filter. Each of these filter portions was then analysed for metals. The percentage deviation of the determined metal levels was calculated for the post-extraction samples relative to the pre-extraction samples. These percentage deviation values for selected metals are shown in

Figure 6.5. Different data point markers as denoted in the legend represent the metals evaluated. We observed a general decrease in the determined metal levels for all air samples. In unusual cases, metals such as titanium, calcium, zinc, vanadium and nickel showed slightly higher levels after extraction in selected samples. Overall, the percentage deviation of metal levels post-extraction ranged between 0 to (–)30% with an average of approximately (-)11%. This data suggests that organic extraction removes a small but significant portion of the metal content from the air samples. It also suggests that the determination of metals in previously extracted filters (i.e., air samples dated prior to 1996) is feasible and will provide valuable information, however, the metal results may not be as accurate as those for unextracted air samples.

6.3.2.2. Metals Levels in Blank Filters

Another important question for metals analyses is the issue of variability and background levels of metals in the filters themselves. Metals levels were determined in different portions of a blank air filter, the results shown in Figure 6.6. Each filter portion was analysed in triplicate; the standard deviations of these analyses were very tight (see error bars in the Y component indicating ± one standard deviation). These "blank" metals levels in the filters were compared to the average metals levels determined for real air samples on a yearly basis. The comparison between the average blank levels (see dotted line) and the average levels detected in 1996, 1997 and 1998 is shown in Figure 6.7; chart (a) has the Y axis on a linear scale and chart (b) has it on a logarithmic scale. The Y error bars on the average yearly determinations are relatively wide due to the large variation in

metal levels in different air samples. The yearly average metal levels are well above the blank levels for metals associated with steel industry impacts such as Mn, Fe, Cu, As, Sn and Pb.

6.3.2.3. Reproducibility of Metals Determinations Across an Air Filter

The reproducibility of metals determinations across an air filter was evaluated by ICP-MS analysis of 14 different portions cut from the same air sample filter (filter #6028, Dofasco 2 site, June 15, 1998) in designated areas (as shown in Figure 6.9). The results are shown in Figure 6.8. The mean for all metals determinations is represented by a percentage deviation of zero. The locations on the air filter where the filter disks were cut are denoted by numbers on the X axis which correspond to the numbered locations in the illustration in Figure 6.9. The results showed that the deviations of individual metal determinations across the filter fell within a range of approximately ± 20%. In qualitative evaluation of a large number of air sample filters, an uneven particulate distribution was indicated on many filters by a variation in color from dark to light going from the middle of the filter outwards. Thus, it was expected that filter portions 1-8 would show positive percentage deviations (indicating higher metal levels) as they were located in the middle of the filter where the particulate is sometimes found to be darker (and expectedly more dense). This was indeed true for the most part for portions 1, 2, 7 and 8, but was not true for portions 3-6. Portions 3-6, 12-14 exhibited mainly negative deviations from the mean metal levels. The metal levels across the filter were not as predictable as we had expected, and did not exhibit symmetrical correlations in general. Manganese exhibited

deviations from the mean ranging from 0.06 to 12.6%. Tin exhibited more variable deviations ranging from 0.26 to 60% due to an unusual level in one filter portion. On average, deviations of metal values from the mean fell within ± 10%. This overall range of deviations is relatively low. Filter portions for ICP-MS analysis in the present research were taken from the same area of each air filter sample (corresponding to areas 1,2,5,6 in Figure 6.9).

ICP-MS analysis duplicates were performed for three air filter samples (filter # 5059, 6016, 6034). The duplicate data exhibited less than 11% deviation from the mean for all duplicates except for one 30% deviation for one Sn determination for filter # 6016. The majority of deviations were below 6% for the duplicate analysis data.

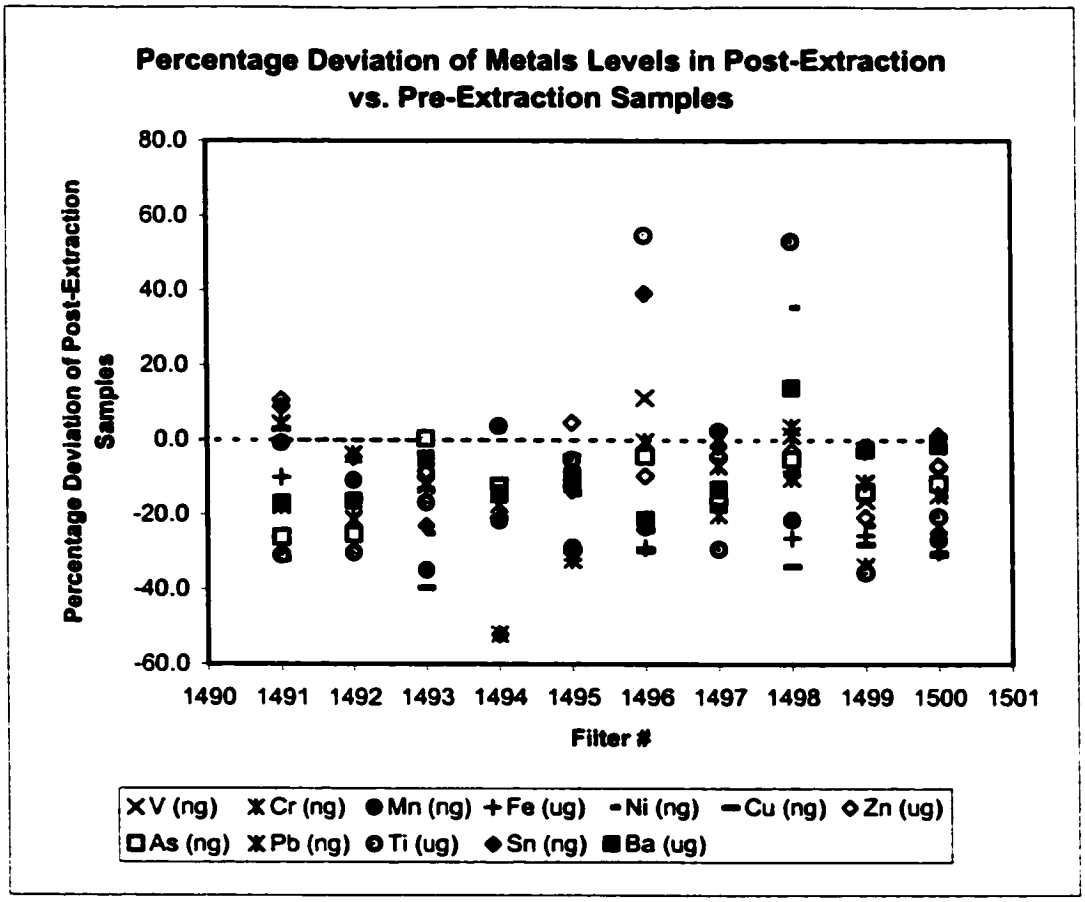


Figure 6.5: Percentage deviation of metals levels in air samples after organic extraction relative to unextracted samples (air samples from 1996 air monitoring campaign).

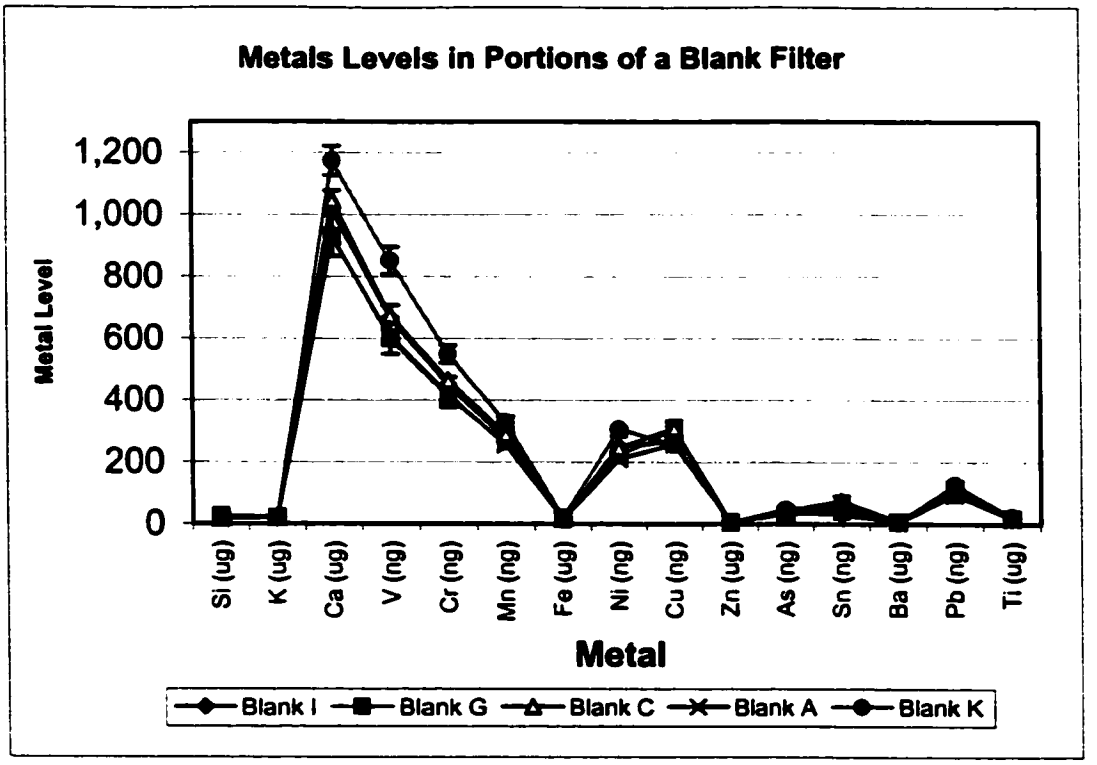


Figure 6.6: Background metals levels in portions of a blank air filter. Each blank sample was analysed in triplicate, the error bars (in the direction of the Y-axis) indicating +/- one standard deviation.

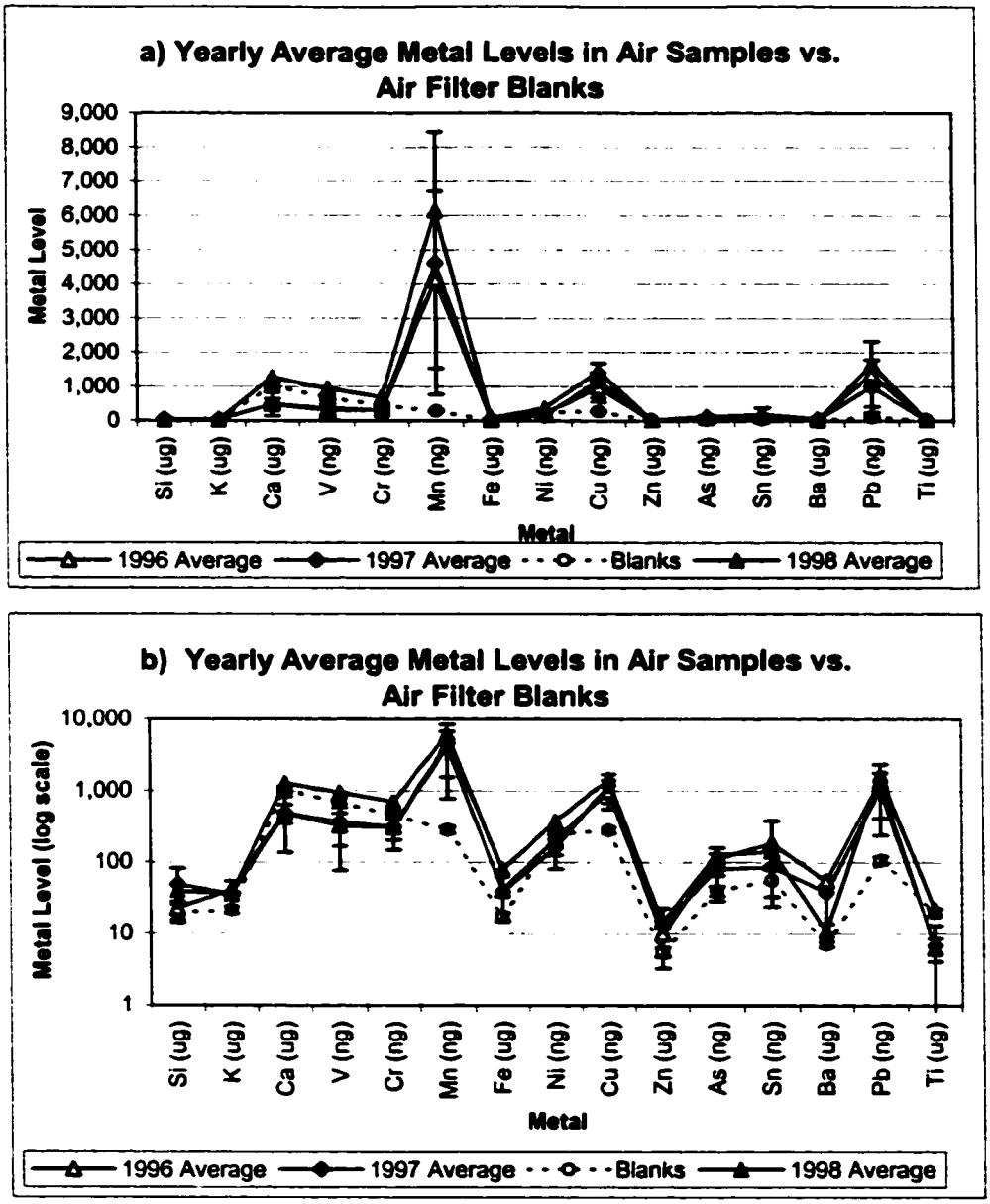


Figure 6.7: Yearly average metal levels in air samples collected in 1996, 1997 and 1998 as compared to blank filter levels, (a) Y axis on a linear scale, and (b) Y axis on a logarithmic scale (Y error bars represent +/- one standard deviation).

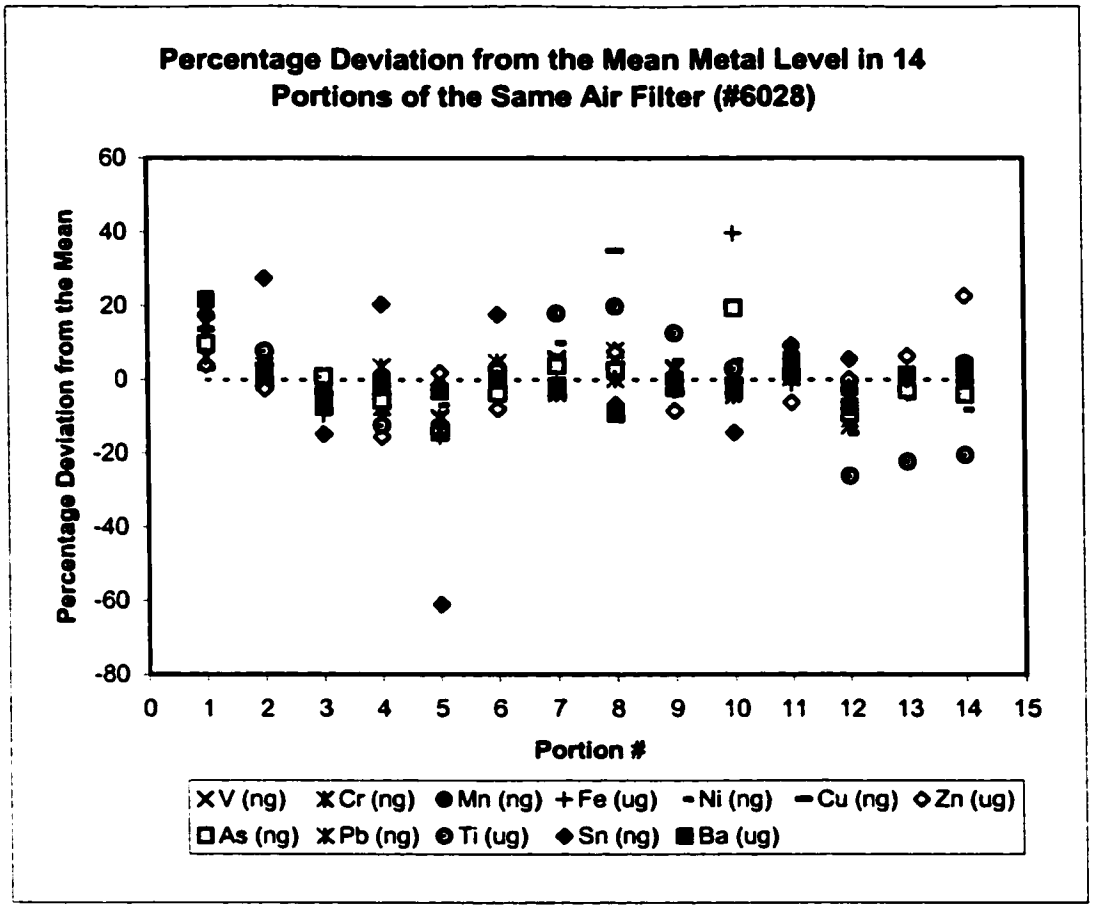
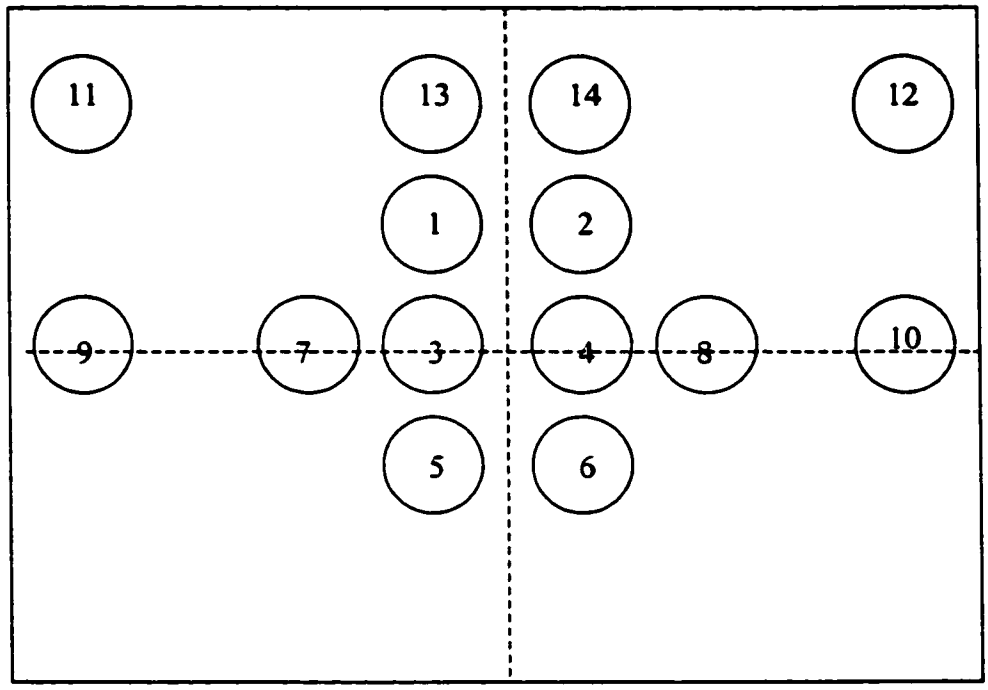


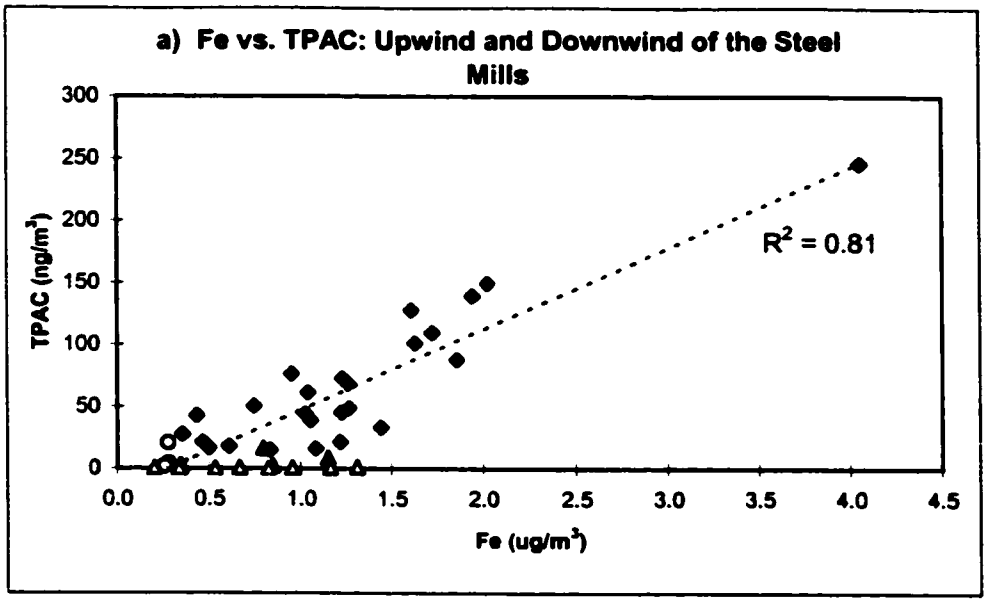
Figure 6.8: Reproducibility of metal level determinations in different portions of one air sample (filter # 6028, 1998 air monitoring campaign). The mean value is represented by a percentage deviation from the mean of 0%.

Figure 6.9: Illustration of the areas of an air sample filter cut in order to assess the reproducibility of metal determinations across a filter. The rectangle represents the portion of the air filter containing air particulate; the dashed lines represent the centre lines on the filter. Disks were cut out of the filter according to the pattern and numbering shown.



6.3.3. Comparisons of PAC and Metals Data

In the figures of this section, each of the air particulate samples was classified according to the level of coke oven impacts based on the total PAH values and the R234 thia-arene ratio. We categorized samples into one of 3 classifications: (a) minimal coke oven impact with R234 > 3.1 (open triangles - 1997/98 data and open circles - 1996 data), (b) intermediate coke oven impacts with R234 near 3.1 (closed triangles - 1996 data), (c) heavy coke oven impacts with R234 < 3.1 (closed diamonds - 1996 data). A plot of the total Fe level ($\mu g/m^3$) versus the TPAC level (ng/m^3) for all of the 1996 ambient air samples is shown in Figure 6.10 (a). The high levels of iron downwind of the steel mills are not surprising given the metallurgical processes and iron processing operations at the steel mills. Samples with low Fe levels have low TPAC levels while samples with high Fe levels have high TPAC levels; these data showed a clear linear trend with $R^2 = 0.81$. The same trend was seen for Mn (Figure 6.10 (b)) with an $R^2 = 0.71$. In a similar fashion, we examined 9 other metals associated with the steel industry (Figure 6.11 to Figure 6.14). The R^2 values were 0.70 for Pb, 0.67 for As and 0.64 for Zn; the other R^2 values are shown in Figure 6.13 and Figure 6.14. The low impact and high impact samples are differentiated best for Mn, Sn, Fe, Pb, and As.



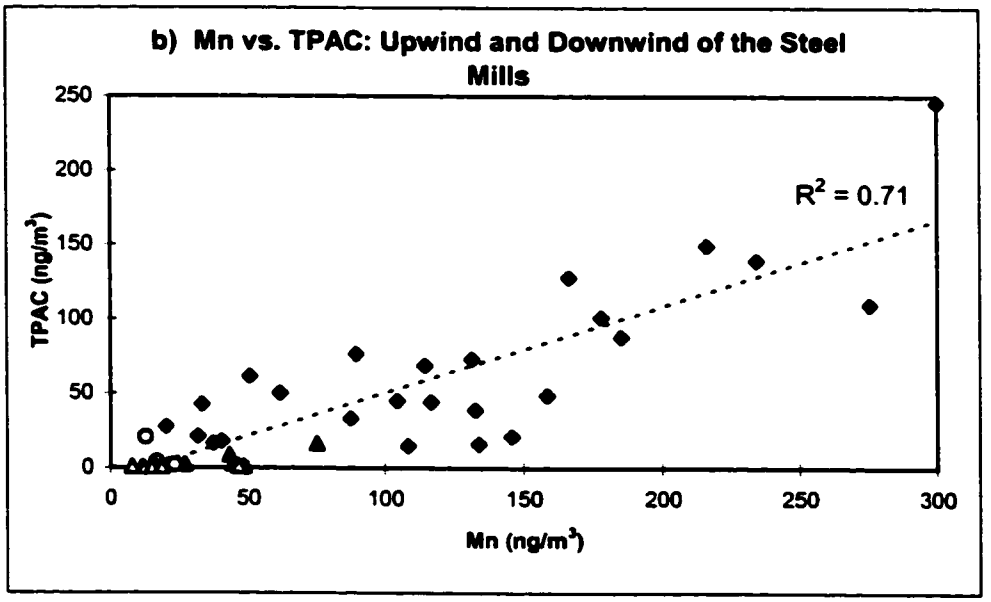
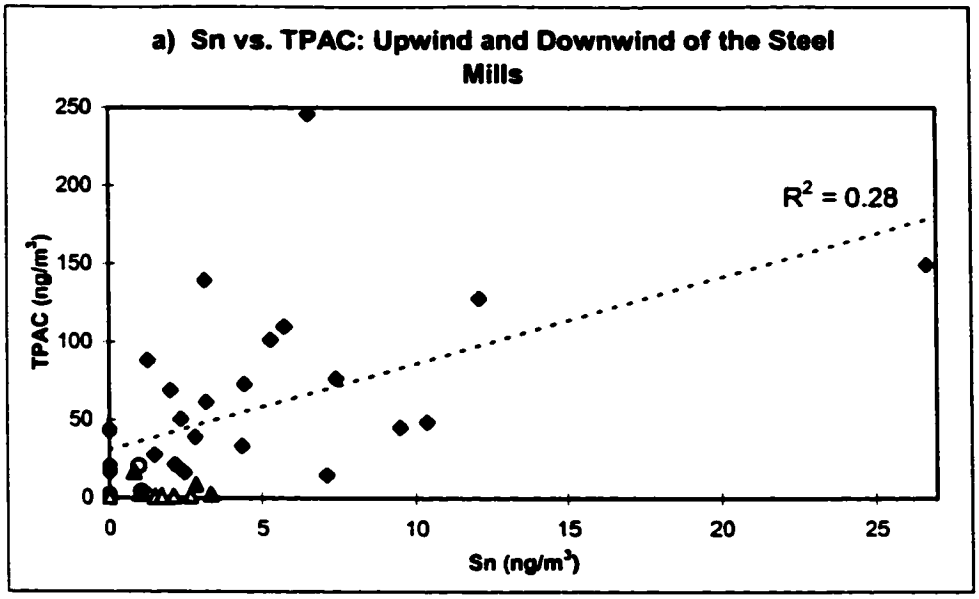


Figure 6.10: Relationship between total concentration of PAC and the amount of (a) iron and (b) manganese, associated with air particulate samples collected upwind and downwind of the steel industry (Minimal Impacts - 1996/open circles, 1997/98/open triangles, Low Impacts - 1996/closed triangles, Heavy Impacts - 1996/closed diamonds).



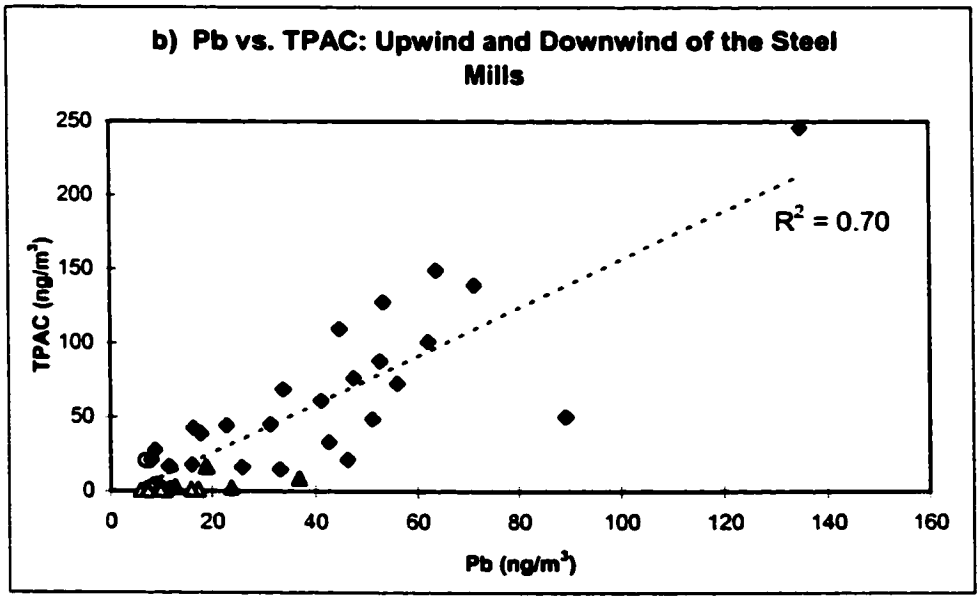
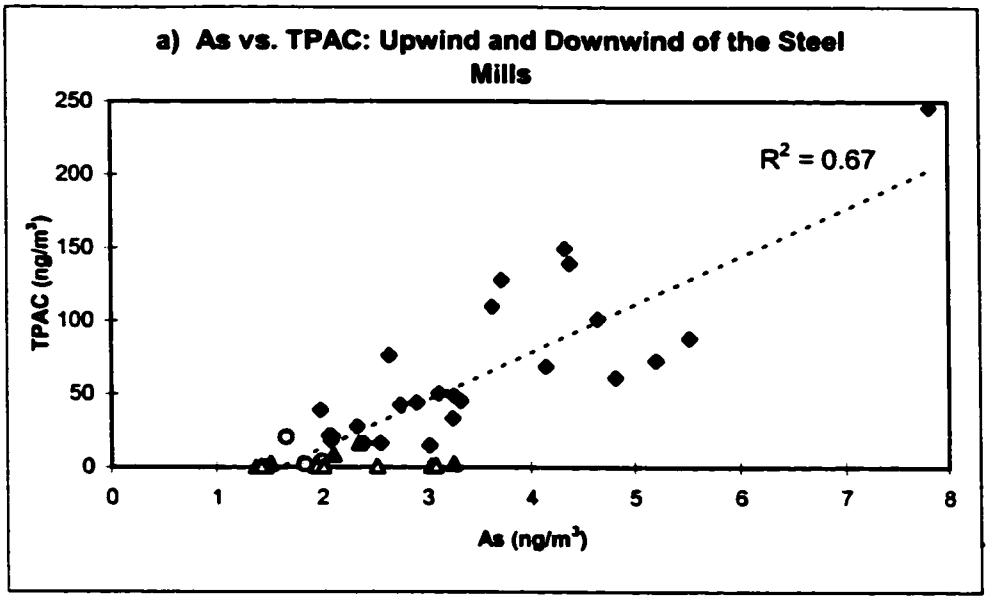


Figure 6.11: Relationship between total concentration of PAC and the amount of (a) tin and (b) lead, associated with air particulate samples collected upwind and downwind of the steel industry (Minimal Impacts - 1996/open circles, 1997/98/ open triangles, Low Impacts - 1996/closed triangles, Heavy Impacts - 1996/closed diamonds).



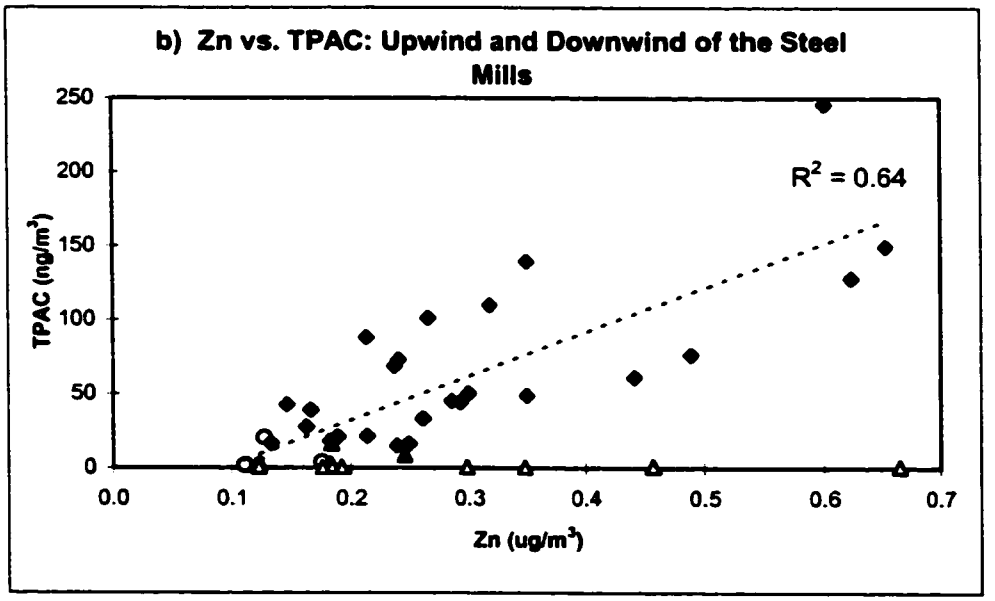


Figure 6.12: Relationship between total concentration of PAC and the amount of (a) arsenic and (b) zinc, associated with air particulate samples collected upwind and downwind of the steel industry (Minimal Impacts - 1996/open circles, 1997/ 98/open triangles, Low Impacts - 1996/closed triangles, Heavy Impacts - 1996/closed diamonds).

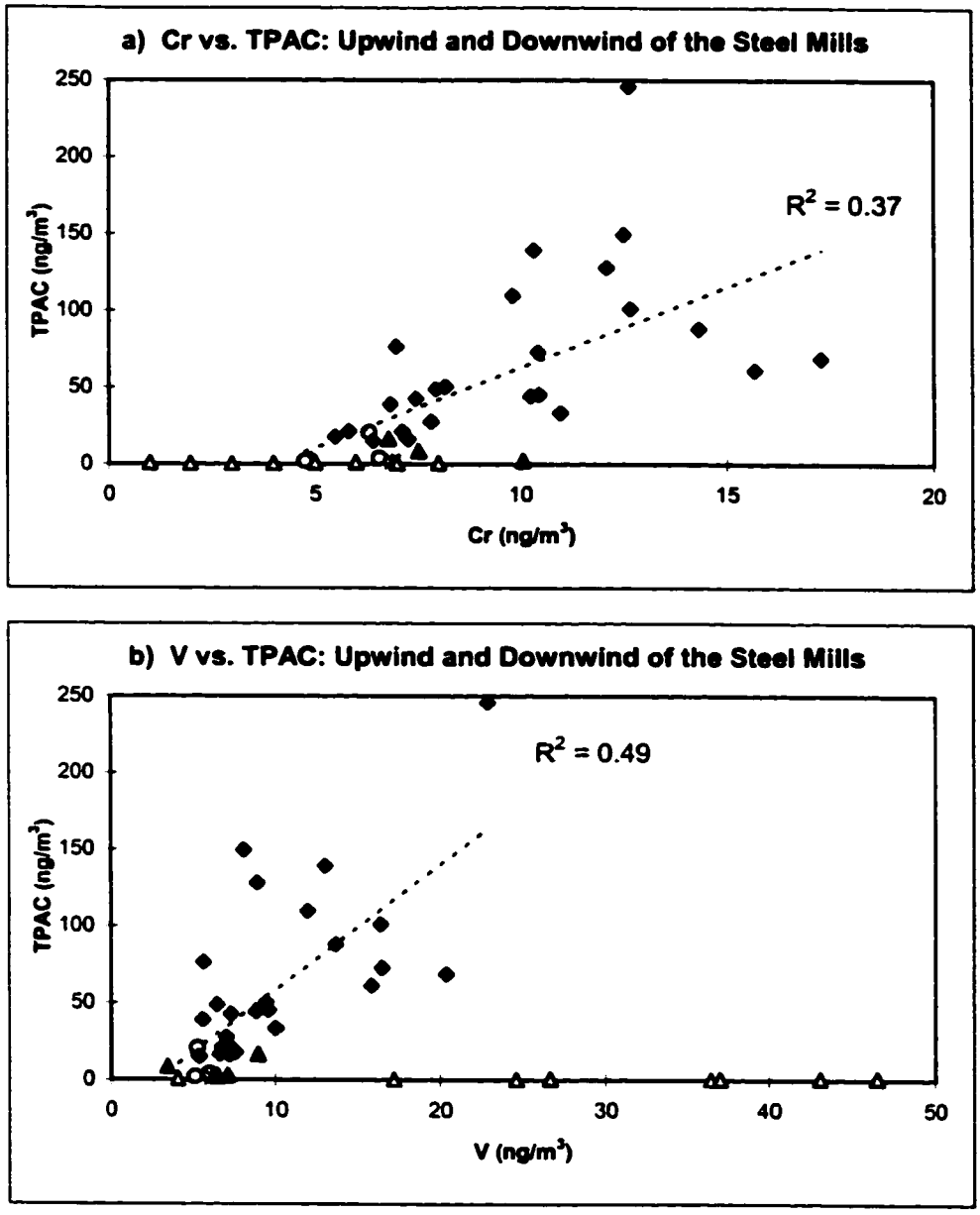


Figure 6.13: Relationship between total concentration of PAC and the amount of (a) chromium and (b) vanadium, associated with air particulate samples collected upwind and downwind of the steel industry (Minimal Impacts - 1996/open circles, 1997/98/open triangles, Low Impacts - 1996/closed triangles, Heavy Impacts - 1996/closed diamonds).

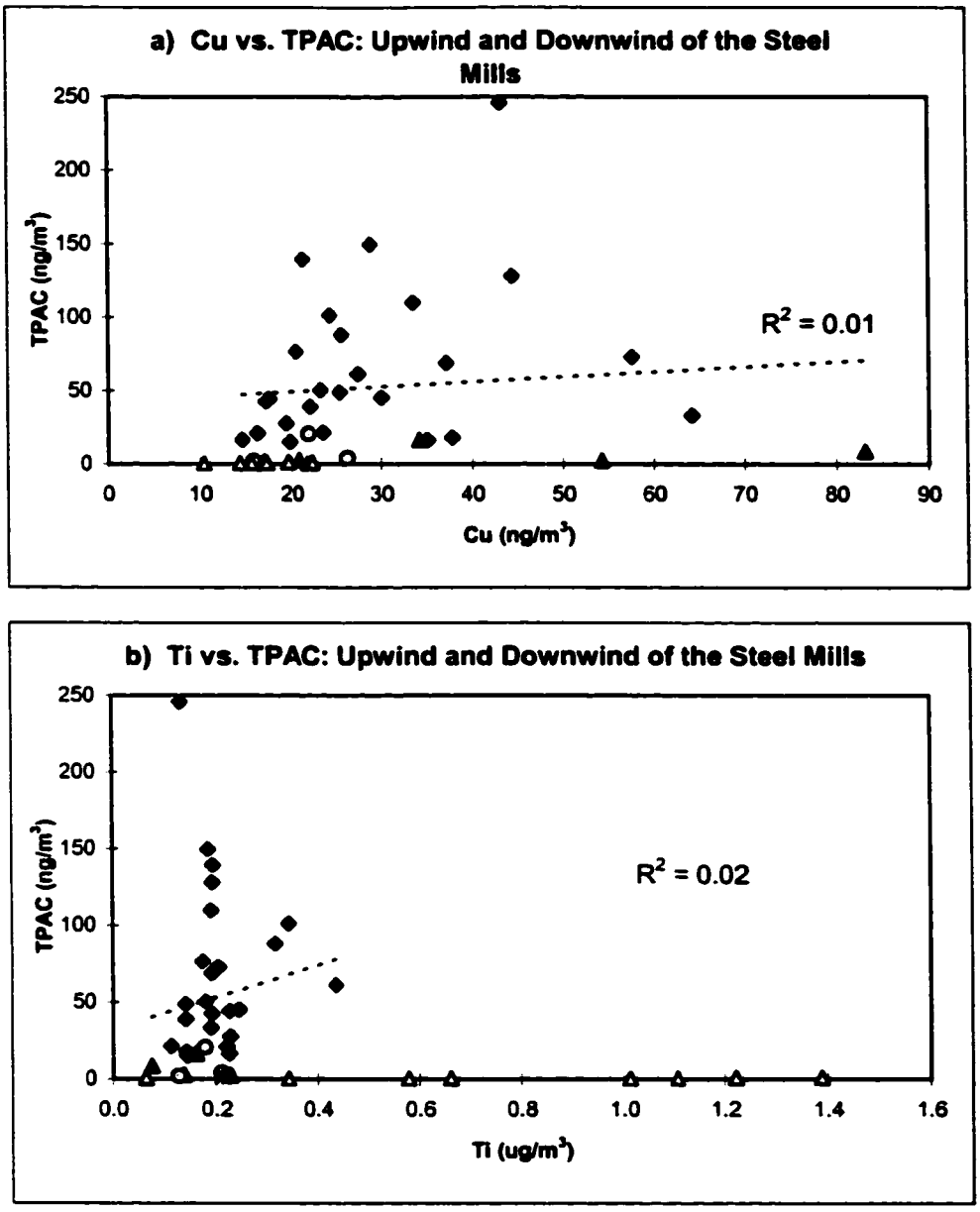


Figure 6.14: Relationship between total concentration of PAC and the amount of (a) copper and (b) titanium, associated with air particulate samples collected upwind and downwind of the steel industry (Minimal Impacts - 1996/open circles, 1997/98/open triangles, Low Impacts - 1996/closed triangles, Heavy Impacts - 1996/closed diamonds).

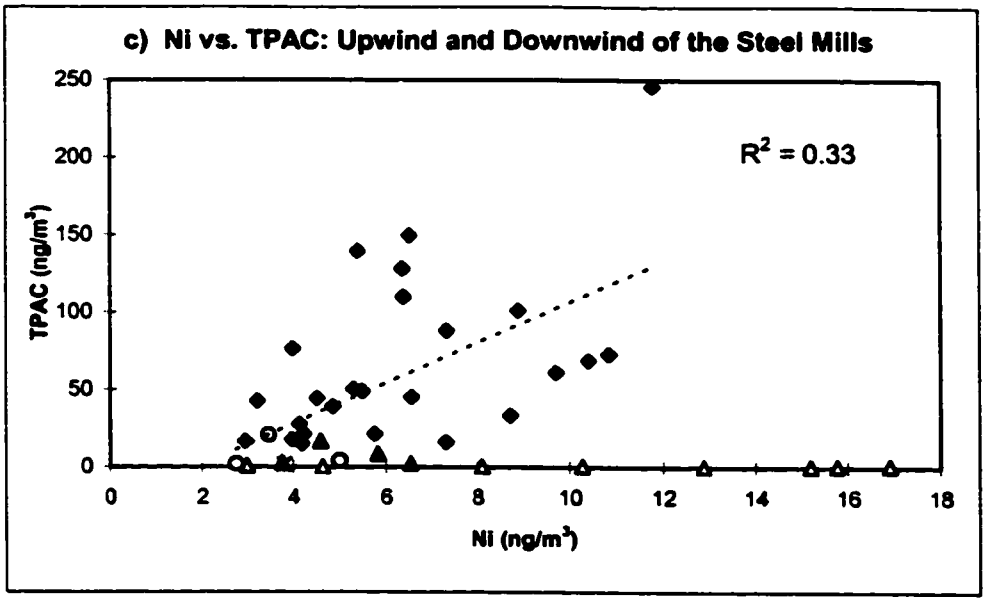


Figure 6.14: (c) Relationship between total concentration of PAC and the amount of nickel associated with air particulate samples collected upwind and downwind of the steel industry (Minimal Impacts - 1996/open circles, 1997/98/open triangles, Low Impacts - 1996/closed triangles, Heavy Impacts - 1996/closed diamonds).

6.4. DEVELOPMENT OF A METAL INDEX SOURCE APPORTIONMENT TRACER FOR STEEL INDUSTRY EMISSIONS

Each of the 11 metals was plotted against total PAC content and a specific value was selected as a "boundary" to differentiate between samples with low impacts versus those with high impacts; this value as a normalization factor for that metal. Each metal value was then divided by the normalization factor. Normalization factors were as follows: As (3.8 ng/m^3), Cr (10.2 ng/m^3), Cu (54.7 ng/m^3), Fe (0.46 μg/m^3), Mn (44.5 ng/m^3), Ni (6.7 ng/m^3), Pb (24.3 ng/m^3), Sn (2.43 ng/m^3), Ti (0.23 μg/m^3), V (7.29 ng/m^3), Zn (0.20 μg/m^3). Using this approach, it was anticipated that air particulate samples that were heavily impacted by steel industry emissions would have normalized metal values greater than 1, while samples with low impacts would have normalized metal values less than 1.

The normalized metal data were plotted against the TPAC data and also against the R234 data in order to determine whether that metal showed promise as a potential source apportionment tracer for steel industry emissions. Figure 6.15 (a) and (b) illustrate the normalized Mn and Sn data plotted versus the TPAC levels for each of the air particulate samples. This data set contains upwind samples from 3 years of sampling; upwind samples collected at Pier 25 in 1996 are shown as open circles, and samples collected upwind at the Pool site in 1997 and 1998 are shown as open triangles.

The majority of the upwind samples had normalized metal values less than one, indicating that they have minimal impacts from the steel industries. The upwind samples also have the lowest total polycyclic aromatic hydrocarbon levels (> 5 ng/m^3), indicating

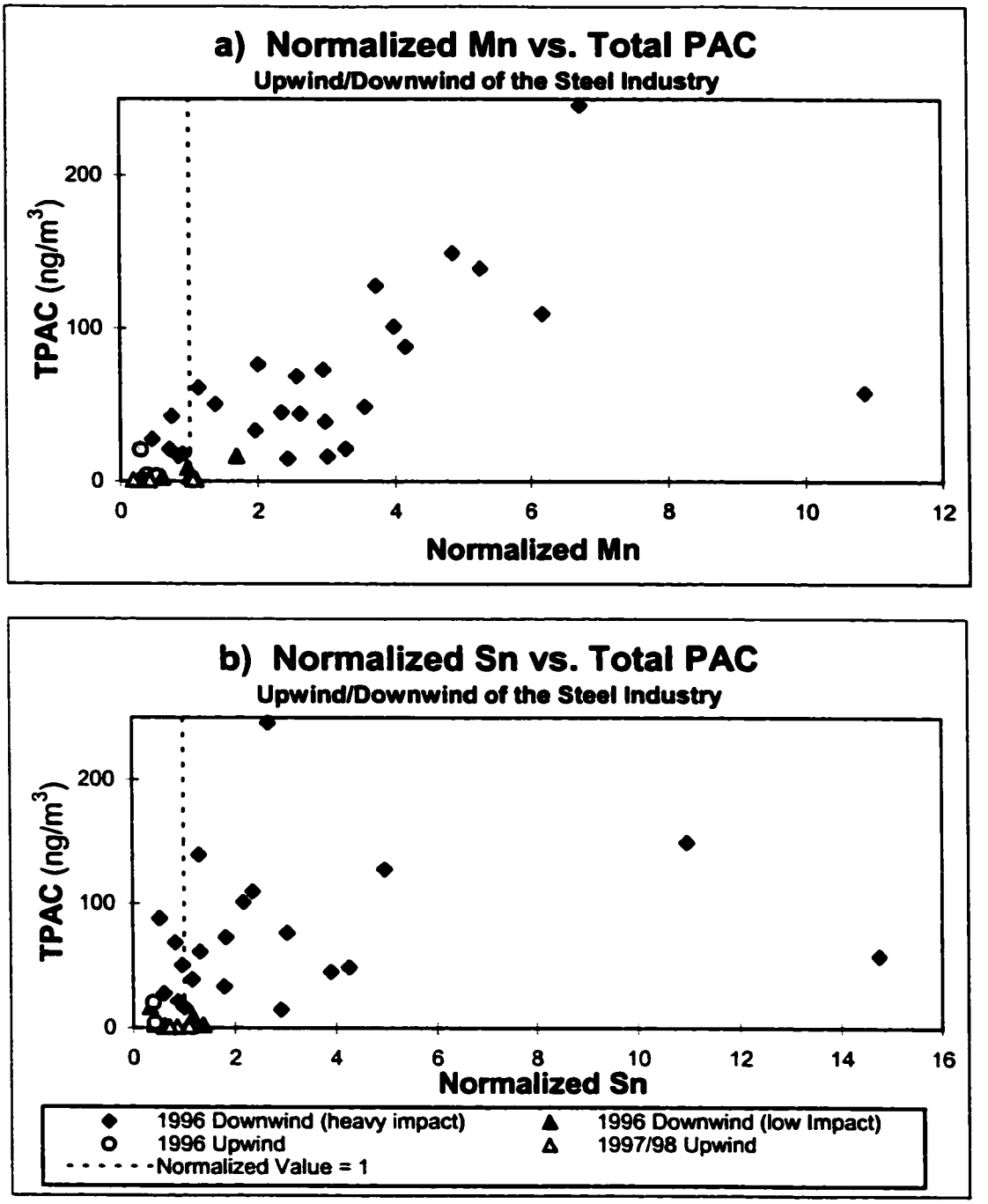


Figure 6.15: Relationship between total concentration of PAC and (a) level of Mn normalized (normalization factor 44.5 ng/m^3) and (b) level of Sn normalized (normalization factor 2.43 ng/m^3). The vertical dashed line represents the normalized value of 1.

that they do not have significant coke oven impacts (L.M. Allan found that air particulate samples with TPAC levels > 5 ng/m^3 showed clear evidence of coke oven emission impacts).[144] On the other hand, samples with normalized metal values > 1 had TPAC levels from 20 - 250 ng/m^3, indicative of significant steel industry/coke oven impacts. The Mn and Sn data are displayed more clearly in Figure 6.16 (a) and (b) which are identical to Figure 6.15 (a) and (b) except that the normalized metal data (X axis) is plotted on a logarithmic scale. Overall, as the total polycyclic aromatic compounds levels (TPAC) increased, so did the normalized metal levels.

The normalized metal data were then assessed to evaluate which of the 11 metal data sets classified the samples the most accurately. Mn and Sn appeared to give the best discrimination and were examined more closely as potential source apportionment tracers. These metals did not give clear differentiations as to source alone, so it was decided to use them in a linear (1:1) combination in order to define a Mn-Sn Metal Index. Manganese is known to be released from iron and steel operations[27,154] and is one of the metals reported as a regular release by Dofasco in the NPRI reports from 1996 to 1998 (3.8 - 6.7 tonnes per year released to the air primarily from their electric arc furnace baghouse and from their basic oxygen furnace). Tin has been associated with coal combustion and the coking process.[154]

In the 1996 data set, 5 out of 26 samples were classified as low impact samples for both Mn and Sn by the normalization procedure. Four of these five data points represented different samples in the two data sets. This observation suggested using both elements together in a linear Mn-Sn index.

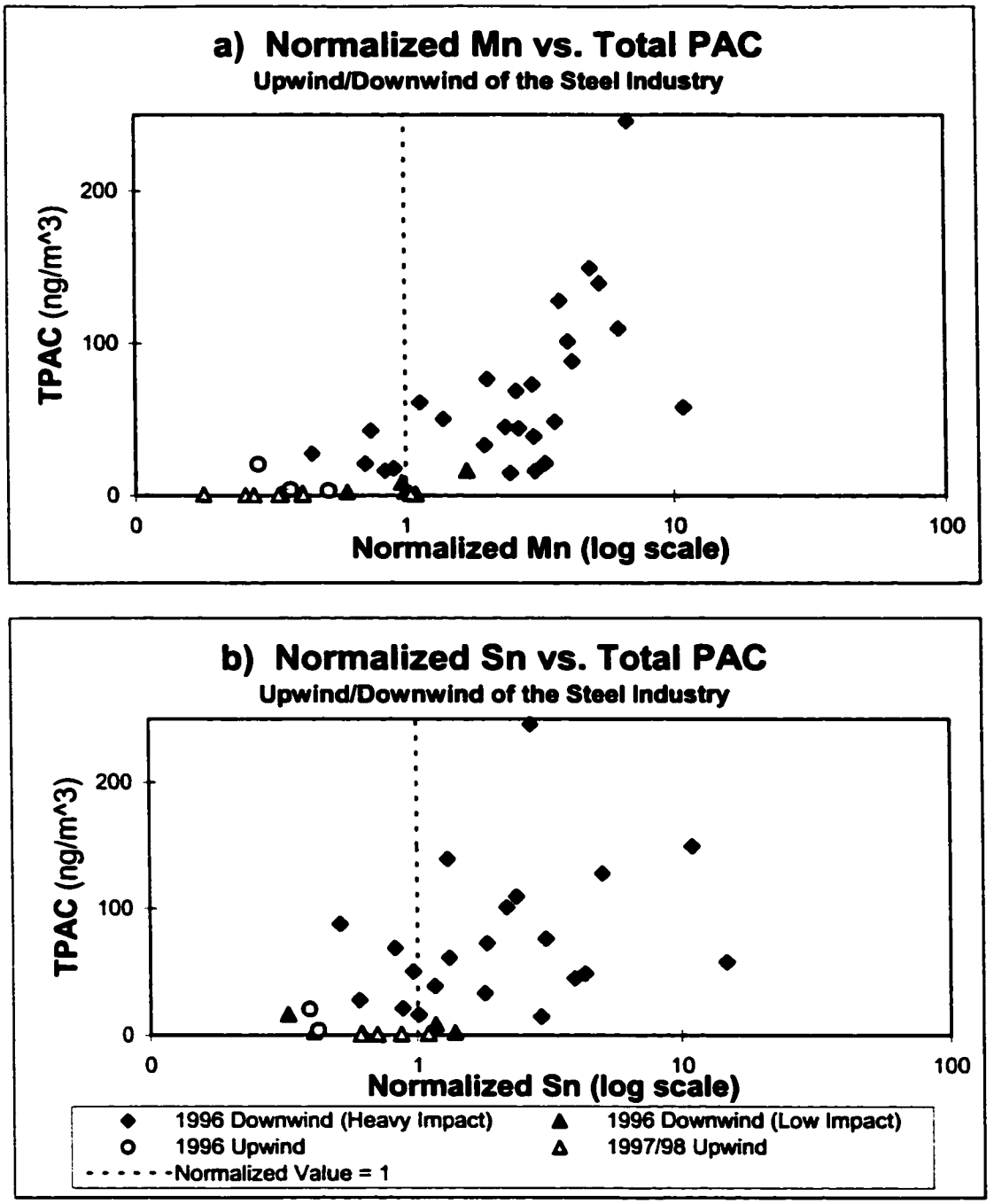


Figure 6.16: Relationship between total concentration of PAC and (a) level of Mn normalized (normalization factor 44.5 ng/m^3 - log scale) and (b) level of Sn normalized (normalization factor 2.43 ng/m^3) on log scale. The vertical dashed line represents the normalized value of 1.

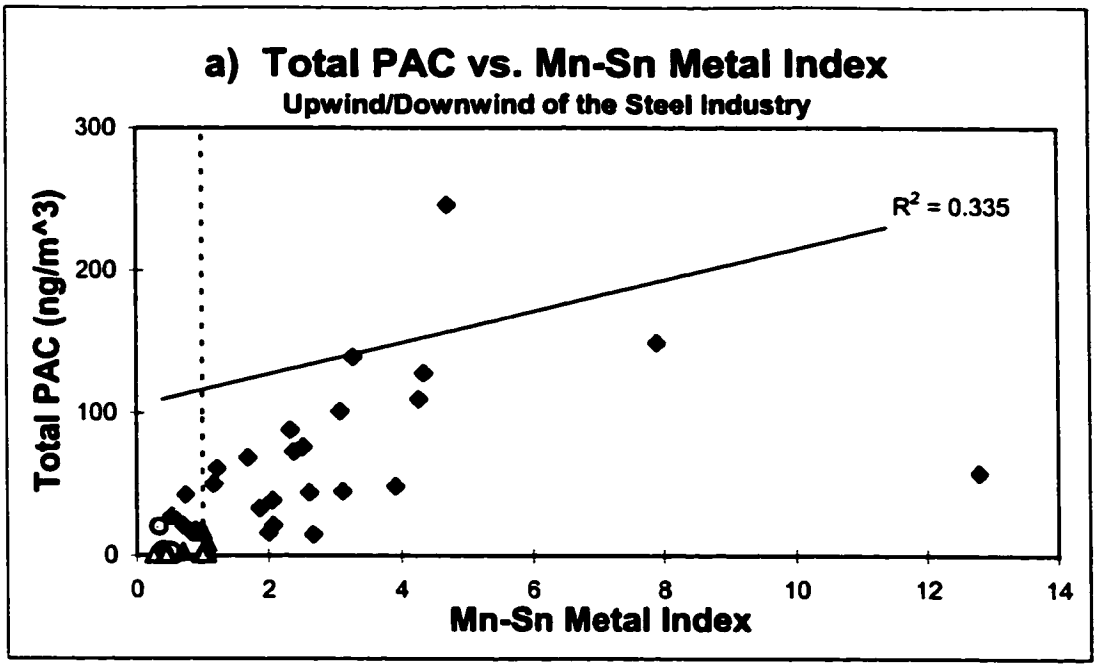
The use of the two metals in a linear combination resulted in the correction of the predictions made using one metal alone. Thus an equally weighted two metal index was created. The Mn-Sn Index is the arithmatic average of the normalized values for Mn and Sn for each air sample. The index is calculated as follows:

$$\text{Mn-Sn Metal Index} = \frac{\left(A_{Mn} / N_{Mn}\right) + \left(A_{Sn} / N_{Sn}\right)}{2}$$

where: A_{Mn} = amount of Mn in air sample (ng/m^3)
A_{Sn} = amount of Sn in air sample (ng/m^3)
N_{Mn} = normalization factor for Mn in air sample (ng/m^3)
N_{Sn} = normalization factor for Sn in air sample (ng/m^3)

Air particulate samples having minimal to low steel industry impacts yielded Mn-Sn Metal Index values below one and those heavily impacted by the steel industry yielded Mn-Sn Metal Index values above one. For 10 of the 44 samples, Sn data was not reported by Activation Labs. For those samples, the normalized manganese values only were used in place of the Mn-Sn Metal Index.

The result of these metal index calculations are illustrated in Figure 6.17 (a) and (b) which are linear and logarithmic plots respectively. In Figure 6.17 (a) a somewhat linear relationship is seen between the TPAC and the Mn-Sn Metal Index ($R^2 = 0.3$). A vertical line was drawn on Figure 6.17 (a) and (b) to show a metal index value of 1 as a guide. The Mn-Sn Metal Index has accurately classified the majority of the samples collected upwind of the steel mills as minimum impact samples (Mn-Sn Index < 1) while the samples collected downwind of the steel mills are heavily impacted samples (Mn-Sn Index > 1).



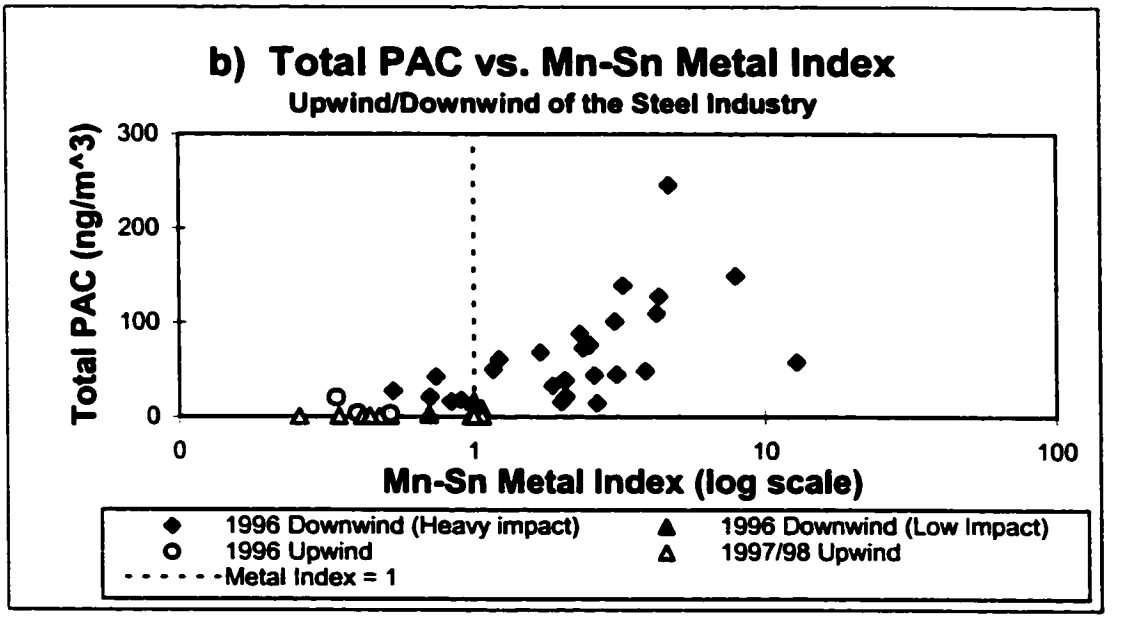


Figure 6.17: Relationship between total concentration of PAC and Mn-Sn Metal Index (a) Metal Index on a linear scale and (b) Metal Index on a log scale, (c) both axes on a log scale. The vertical dashed line represents the normalized value of 1.

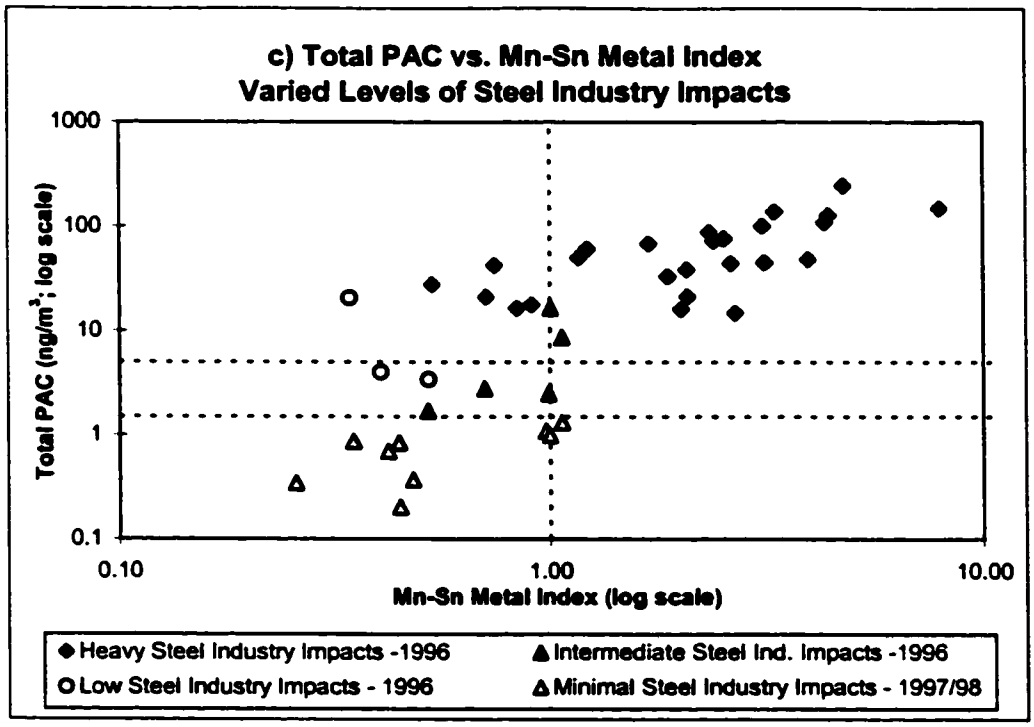
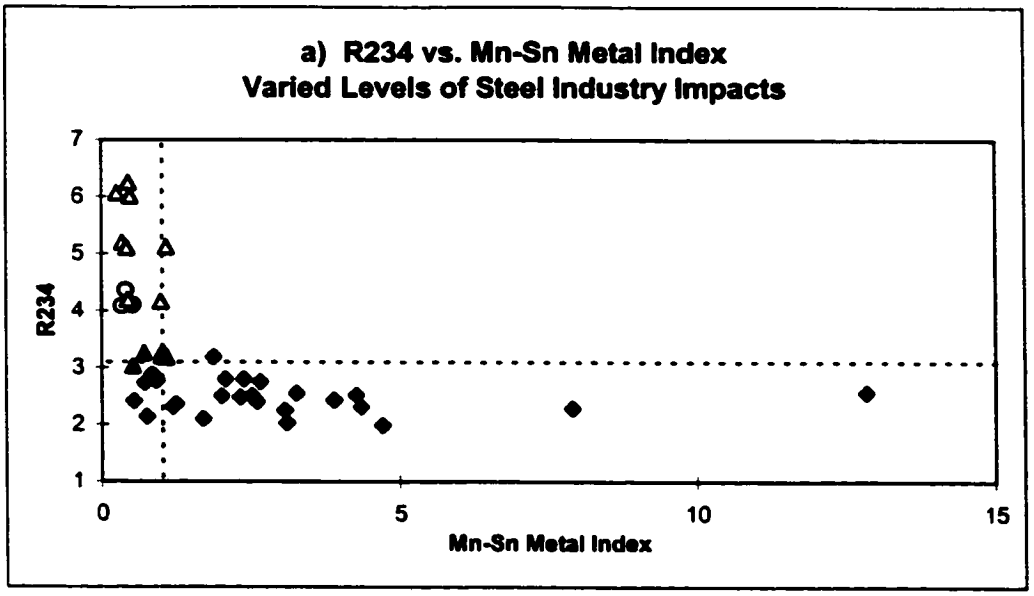


Figure 6.17: c). Relationship between Mn-Sn Metal Index (log scale) and total PAC (log scale) for air samples with varied steel industry impacts. The vertical line represents a Metal Index = 1 and the horizontal line, a TPAC = 1.5 - 5 ng/m^3.

6.4.1. PAC and Metals Data Combined for Source Apportionment

The classification of the remaining samples became clearer when the data were plotted in Figure 6.17 (c) and Figure 6.18. The plot of TPAC level on a logarithmic scale (Figure 6.17 (c)) and the thia-arene R234 ratio on a linear scale (Figure 6.18) when plotted separately against the Mn-Sn Index showed clear separations in the data.

In Figure 6.17 (c), there is a somewhat linear relationship between TPAC and the Mn-Sn Metal Index. This figure offers a classification of air samples in two dimensions: the metal index classification (as described above) and the total polycyclic aromatic compound classification. The lower horizontal dotted line defines a TPAC value of 1.5 ng/m^3 below which samples do not have any significant coke oven impacts[144]. The upper horizontal line defines a TPAC value of 5 ng/m^3, above which samples have measurable coke oven impacts. The samples having metal index values above 1 (indicating heavy steel industry impacts) and TPAC levels above 5 ng/m^3 (indicating coke oven emissions) are classified as having heavy steel industry impacts and lie in the upper right section of Figure 6.17 (c). Samples having metal index values below 1 (indicating minimal steel industry impacts) and TPAC levels below 1.5 ng/m^3 lie in the lower left section and are classified as having minimal steel industry impacts. The remaining air particulate samples with TPAC above 1.5 ng/m^3 and metal index values < 1 are considered to have mixed source contributions using these criteria.



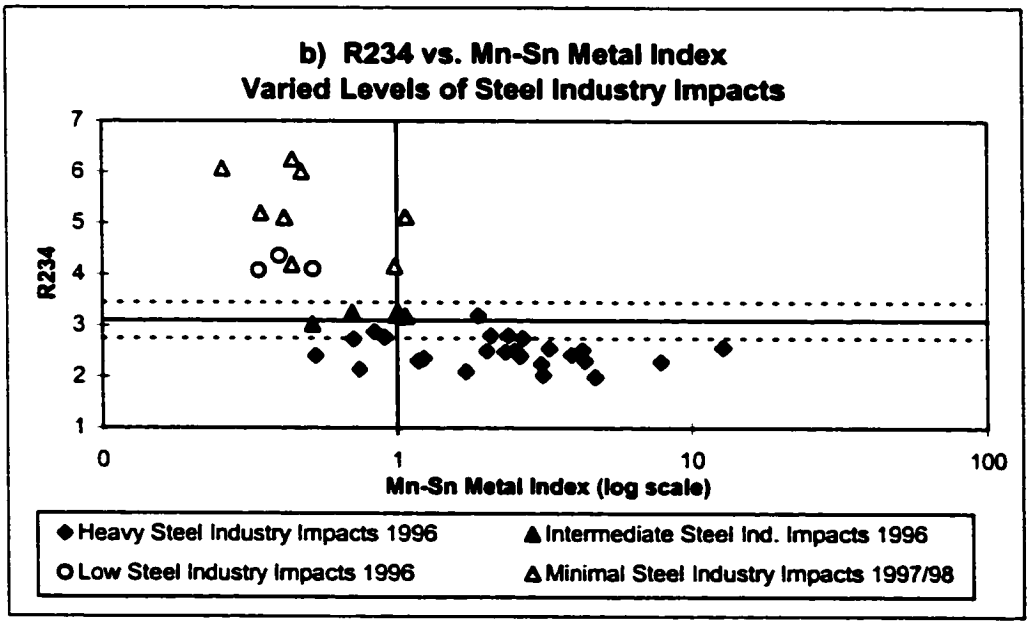


Figure 6.18: Relationship between the 234 amu thia-arene ratio and Mn-Sn metal index: (a) metal index on a linear scale and (b) metal index on a log scale, for air samples having varied levels of steel industry impacts. The vertical lines represent a Mn-Sn Index = 1.0, and the horizontal lines, an R234 = 3.1 +/- 0.35.

The thia-arene R234 ratio was also explored in combination with the Mn-Sn metal index as a potential two-dimensional source apportionment method for steel industry emissions. The relationship illustrated in Figure 6.18 is very similar to that seen in the work of L.M. Allan where the R234 ratio was plotted against total concentration of PAH and against the log of the total PAH concentration (see Figure 6.2). In Allan's plots, a non-linear relationship was observed; the thia-arene ratio decreased rapidly then plateaued with increasing PAH concentrations.[144] At total PAH concentrations above 5 ng/m^3 the thia-arene ratio remained constant. Plots analogous to L.M. Allan's for the present data are shown in Figure 6.18, however, the total concentration of PAH on the X axis has been replaced by the Mn-Sn Metal Index. A similar relationship is found in our plots as was found by Allan. The thia-arene ratio decreased rapidly to values below 3.1 until Mn-Sn Metal Index values exceeded 1. This relationship parallels that observed between thia-arenes and polycyclic aromatic compounds and shows that this metal index is a promising source apportionment tracer for steel industry emissions. Used in combination, the thia-arene ratio and the Mn-Sn Metal Index could be a very powerful two-dimensional source apportionment tool.

Similar relationships in the R234 vs the metal index profile (our method) and R234 vs TPAC profile (Allan's method) are shown in Figure 6.19 (linear scale) and Figure 6.20 (log scale). The metal index plots (Figure 6.19 (a) and Figure 6.20 (a)) are the upper plots of each figure and the TPAC plots (analogous to Allan's work) for the same data are the lower plots. The linear scale plots (Figure 6.19) showed similar trends, however, in the Allan-style plot, two of the air samples collected upwind of the steel mills

(open circles) are unusual in that they have R234 values of about 4 but rather high TPAC values (about 20 and 60 ng/m^3 respectively). These upwind samples have R234 ratios indicative of petrogenic impacts but have TPAC levels indicative of coke oven impacts. These samples are, however, correctly classified using the metal index in the upper plot (Figure 6.19 (a)).

Figure 6.20 illustrates the same plots on a logarithmic scale. In the upper metal index plot, the air samples having minimal steel industry impacts are located in the upper left section (R234 > 3.1 and Mn-Sn index <1) and the samples having heavy steel industry impacts are in the lower right section. In summary, of the 41 data points, all except 12 were assigned as having low or high impact. Some of the data points in the Mn-Sn index = 1 region had R234 values both above and below 3.1. These points lie in a narrow region bordered by Mn-Sn index values of 0.7 and 1.3. Thus, we propose the following criteria for steel industry impacts based on Mn-Sn index values:

	Mn-Sn Index	R234
Low Impact:	< 0.7	> 3.45
Intermediate Impact:	0.7 - 1.3	2.75 - 3.45
High Impact:	> 1.3	< 2.75

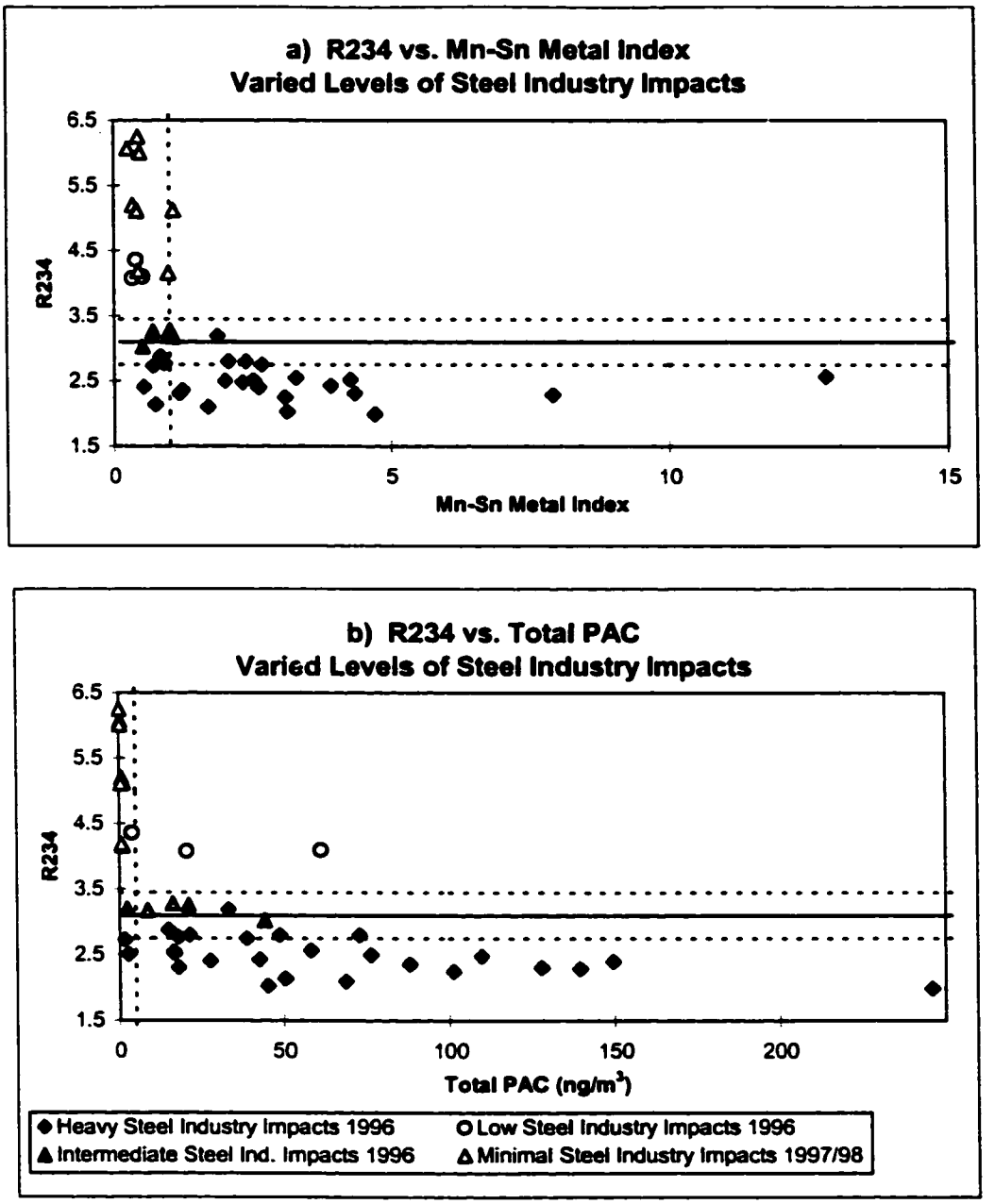


Figure 6.19: Relationship between the 234 amu thia-arene ratio and (a) Mn-Sn metal index and (b) total concentration of PAC for air samples having varied levels of steel industry impacts. The vertical lines represent a) the Mn-Sn Index = 1.0, and b) Total PAC = 5 ng/m^3; the horizontal lines, an R234 = 3.1 +/- 0.35.

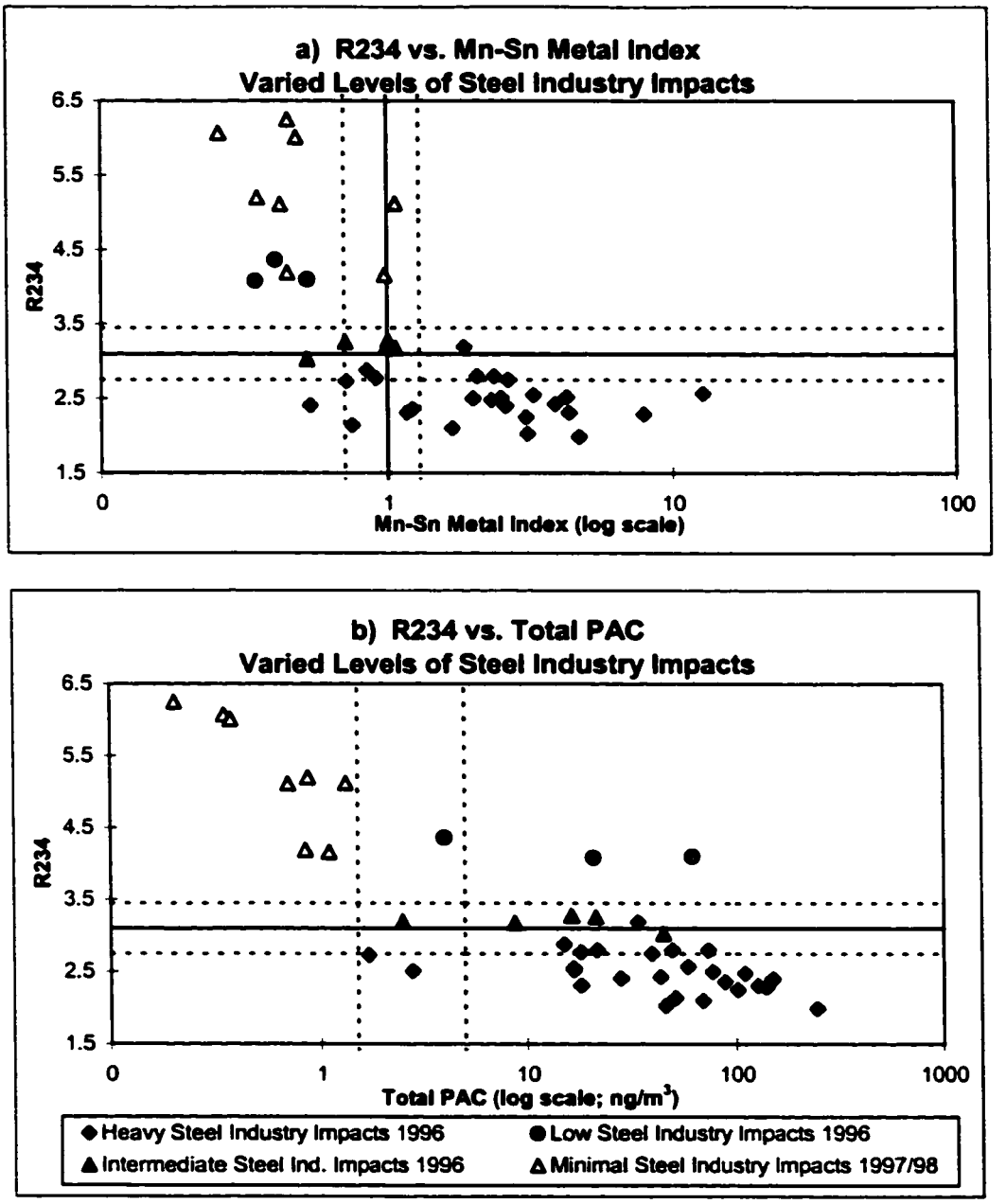


Figure 6.20: Relationship between the 234 amu thia-arene ratio and (a) Mn-Sn Metal Index (log scale) and (b) total concentration of PAC (log scale) for air samples having varied levels of steel industry impacts. The vertical lines represent: a) Metal Index = 0.7 - 1.3, and b) TPAC = 1.5 - 5 ng/m^3 and the horizontal lines, an R234 = 3.1 +/- 0.35.

Overall, in Figure 6.20 (b) a horizontal line defines an R234 ratio of 3.1 ± 0.35, a region below which samples are defined as having coke oven impacts.[144] In Figure 6.20 (a), there are three vertical lines and three horizontal lines. The solid lines represent the divisional values of R234 and Mn-Sn Indices while the dashed lines represent the error ranges associated with each index. Samples having metal index values above 1.3 and R234 ratios below 2.8 lie in the lower right section of the figure, are now classified as having heavy steel industry impacts. On the other hand, air particulate samples having metal index values below 0.7 and R234 ratios above 3.4 are found in the upper-left section of the Figure and are classified as having minimal steel industry impacts. We propose that the samples having data points in the intermediate sections of the plot be considered to have a range of mixed source contributions. These mixed sources may be derived from both diesel and steel industry impacts or from re-entrainment of pollutant-containing dusts from roads, the ground or other industrial fugitive emissions.

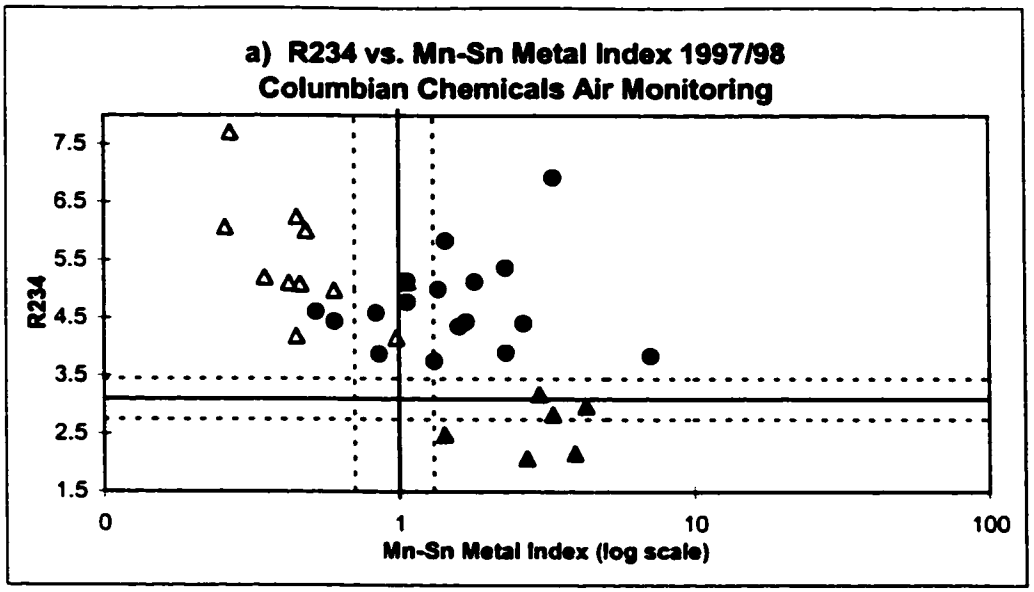
Based on the data from samples collected upwind and downwind of the steel industries, it is clear that the Mn-Sn Metal Index shows good promise as a source apportionment tracer for steel industry emissions. The application of this metal index for samples collected during the 1997 and 1998 air monitoring campaigns near Columbian Chemicals is described below and provides an opportunity to examine this metal index in a somewhat broader context.

6.5. APPLICATION OF THE Mn-Sn METAL INDEX APPROACH

In this section, we will assess the organic and inorganic source apportionment tracers described above by evaluating samples that were not expressly collected near the steel industry. The 1997 and 1998 samples were collected in industrial and residential areas in east Hamilton in order to monitor carbon black emissions. From the ICP-MS data for each filter, Mn-Sn Metal Index values were calculated as described previously. In addition, TPAC levels and thia-arene R234 ratios in the dichloromethane extracts were determined.

These data were plotted as described above, with the R234 ratio as the Y axis and (a) the Mn-Sn index or (b) TPAC as the X axis (see Figure 6.21). Over 85% of the samples had R234 values above 3.45 (indicative of petrogenic impacts), indicating that about 85% of these air particulate samples were not impacted by the coke ovens. Only 6 of the 34 samples (15%) had R234 values less than 3.45 and only 3 had R234 values less than 2.75; these samples also had metal index values above 1.3, consistent with coke oven impacts. Thus, this data set is very different from the 1996 data set discussed above.

We have classified all of the 1997/98 Columbian monitoring samples according to Allan's source apportionment work in Figure 6.21 (b). The open triangles were classified as samples of petrogenic origin. The closed triangles are indicative of steel industry coke oven impacts.



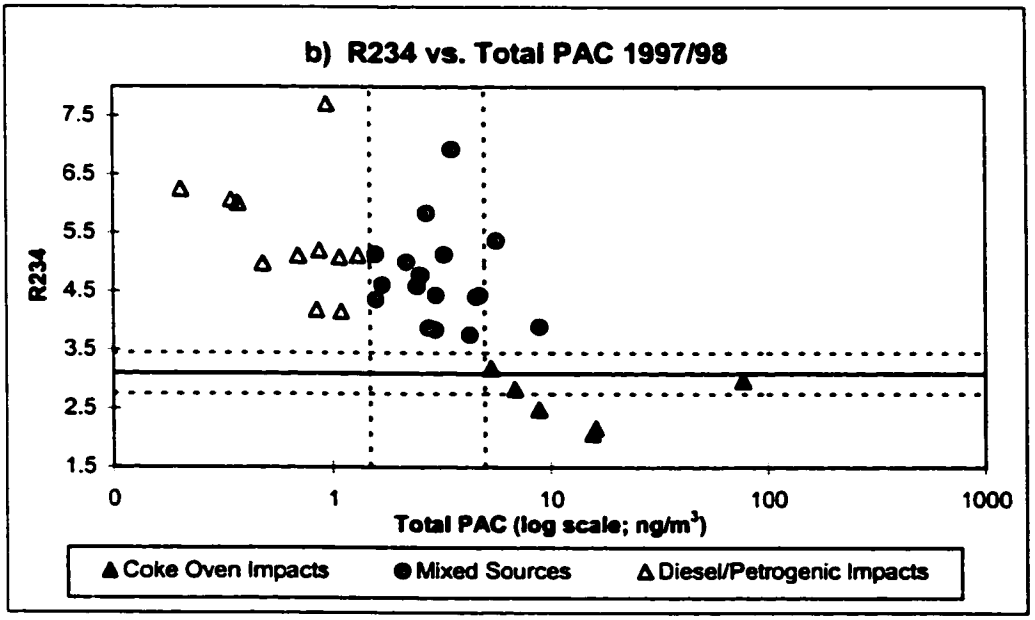


Figure 6.21: Relationship between the 234 amu thia-arene ratio and (a) Mn-Sn Metal Index (log scale) and (b) total concentration of PAC (log scale) for all air samples collected in 1997 and 1998 during the carbon black air monitoring campaigns. The vertical lines represent a) Metal Index = 1 +/- 0.3, and b) TPAC = 1.5 - 5 ng/m^3 and the horizontal lines, an R234 = 3.1 +/- 0.35.

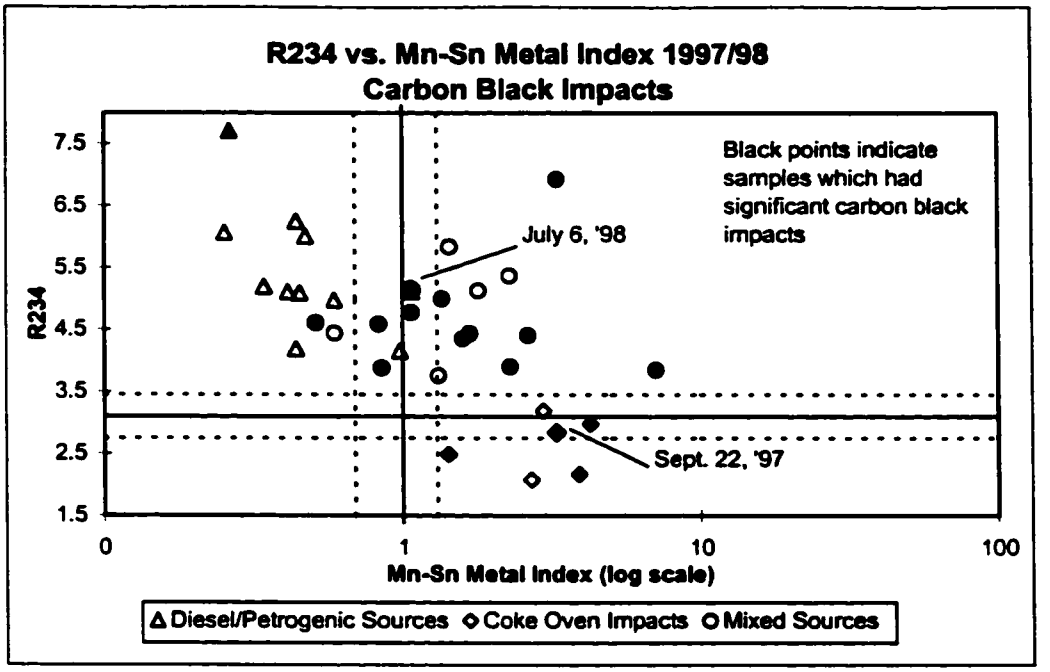


Figure 6.22: Relationship between the 234 amu thia-arene ratio and the Mn-Sn Metal Index (log scale) for all air samples collected in 1997 and 1998 during the carbon black air monitoring campaigns. The air samples having carbon black impacts are indicated as black data points.

The remainder of the air samples in grey circles are classified as having mixed source contributions according to Allan's approach. If we map those same data points with these classifications onto a plot using the Mn-Sn index approach, we get the upper Figure 6.21 (a). Again, in this Figure, the samples with minimal steel industry coke oven impacts (open triangles) lie in the upper left section (where R234 > 3.1, metal index < 1), and the more heavily impacted samples (closed triangles) lie in the lower right section.

The samples represented as grey circles are classified by the metals approach as having mixed source contributions, as in Allan's approach. These samples may contain particulates derived from the steel industry as well as particulates derived from petrogenic fuel combustion. Manganese has been widely used in antiknocking agents (MMT or (η^5-$CH_3C_5H_5$)$Mn(CO)_3$)) as a replacement of lead derivatives in vehicular fuels. Those samples represented by grey circles, having R234 ratios indicative of petrogenic fuel combustion and high metal index values may be due in part to vehicular emissions from the combustion of manganese-containing petroluem products. This theory could be tested in future research using air samples containing vehicular emissions.

It is interesting to see which of these air samples in Figure 6.21 were determined to have carbon black impacts in our carbon black monitoring campaign. We have indicated those samples which were found to have carbon black impacts as closed (black) data points in Figure 6.22. The two samples that had the greatest carbon black impacts had rather different metal index and R234 values (July 6, 1998 and September 22, 1997) as indicated in Figure 6.22. This figure shows that air samples with carbon black impacts

are found throughout the chart, indicating that there is no correlation between impacts of carbon black and impacts derived from the steel industry or petrogenic fuel combustion sources.

6.5.1. Utility of the Metal Index

The metal index approach could potentially be used on its own as a tool to determine the level of steel industry impacts in ambient air samples. By performing ICP-MS analyses on a small portion of an air particulate sample and calculating the Mn-Sn metal index, one can identify whether the sample has little impact or heavy impacts from steel industry sources based on the value of the metal index (< 0.7 or > 1.3 respectively). The metal index approach could thereby be used as a screening tool for the presence of steel industry impacts; this preliminary metal index analysis would aid in sample selection and reduction in sample load for the more lengthy and costly organic analyses.

This preliminary evaluation of the use of metals versus PAC and thia-arene data in source apportionment has shown that the metal index has achieved equivalent efficacy in the source apportionment of steel industry emissions. Overall, the Mn-Sn metal index has been found to be a valuable tool in differentiating air samples with minimal pollution impacts, and those having heavy steel industry impacts or mixed source contributions. Married with the R234 ratios, the Mn-Sn metal index provides a 2-dimensional source apportionment method that can evaluate the levels of steel industry impacts in ambient air samples. We therefore encourage further research in the use of the Mn-Sn index as a

source apportionment tool, and a potential screening tool for steel industry impacts in ambient air samples.

7. CONCLUSIONS AND FUTURE WORK

A new method has been developed for the identification and determination of carbon black in ambient air particulate. Thiacoronene, a 306 Da sulfur-containing PAC found in many carbon blacks, was used as a source tracer for carbon black in air particulate. In a three-year field study, low but easily determined levels of carbon black were detected downwind of a carbon black plant. The detection limit for this method is very low (0.004 μg carbon black per m^3 of air) and the method is well-suited to the sampling and analysis of ambient air.

Thiacoronene was found to be associated with background air particulate (air particulate which contains insignificant industrial impingement) at very low levels (average = 0.12 ± 0.11 pg/m^3). These levels are well below the thiacoronene levels found in the toluene extracts of air collected downwind of Columbian; the thiacoronene levels downwind varied between 0.32 and 21.5 pg/m^3 with the majority of levels above 1.0 pg/m^3. Calculations of ambient carbon black levels are based upon "net" thiacoronene levels (downwind minus upwind samples) which subtracts out background contributions.

No significant interferences were found in a range of potentially interfering environmental matrices, or in any chemical or analytical aspects of the method. Through the GC-MS analyses of the organic extracts of various source samples, two additional 306 Da peaks were found which did not interfere with the thiacoronene analysis. These extra peaks were well-resolved from thiacoronene, providing no chemical interferences to the

carbon black method. These 306 Da peaks were found to be associated with samples of diesel particulate (SRM 1650) and coking-related source samples. It may prove valuable in future work to identify these compounds and to identify the sources generating them. These compounds may also prove to be valuable in further source apportionment research.

Hamilton is a very complex environment and the siting of Columbian Chemicals provided unique challenges in terms of potential source contributions. We have evaluated the relationship between thiacoronene levels in the extracts and the total PAC levels of source samples other than carbon black. Knowing this relationship, we were able to assess the potential interferences of these source samples in carbon black determinations. Our findings show that using our sequential extraction method, the levels of thiacoronene in the toluene extracts of industrial source samples are negligible in comparison to those levels in carbon black. In source samples that do contain thiacoronene, the majority of thiacoronene (>90% in general) is efficiently extracted by dichloromethane. From these evaluations, we concluded that the thiacoronene content of a variety of local source samples other than carbon black does not interfere with our method, thereby making thiacoronene a useful marker for carbon black in ambient air particulate.

Our data for carbon black monitoring from the 1995 - 1998 air sampling campaign show that average releases of carbon black from Columbian Chemicals Canada Ltd. in 1997 and 1998 have decreased relative to the average releases found in 1995.

Concentrations of carbon black about 300 m downwind of the plant in July 1995 varied from 0.06 to 1.43 μg carbon black/m^3 of air (average = 0.62 ± 0.47 μg carbon black/m^3). In 1997, concentrations of ambient carbon black collected 1.5 km downwind of the plant were low and varied from 0.02 to 0.97 μg carbon black/m^3 of air (average = 0.22 ± 0.42 μg carbon black/m^3). In 1998 the values were in the same range (0.01 to 1.12 μg carbon black/m^3 of air; average = 0.14 ± 0.31 μg carbon black/m^3: Table 4.6). All concentrations of carbon black were well above our method detection limit of 0.004 μg/m^3. The period of sampling in 1995 prior to the plant renovations yielded the highest carbon black impacts (July 23, 1995, 1.43 μg/m^3; August 2, 1995, 1.26 μg/m^3 at the sampling site (Table 4.1)) as well as the most frequent significant impacts overall. There were also significant impacts in 1997 and 1998, however, the majority of the impacts were low except for those on September 22, 1997 (0.97 μg/m^3) and July 6, 1998 (1.12 μg/m^3). High ambient carbon black concentrations detected at the sampling sites must be the result of some fugitive or accidental release of carbon black from the plant.

Our data from this three year study show that, except for occasional events, fugitive emissions of carbon black from Columbian Chemicals detected at our sampling sites in 1997 and 1998 are lower compared to the 1995 values. The levels of average ambient carbon black concentrations at our sampling sites and the frequency of relatively high carbon black impacts have decreased since the start of the refurbishment of the plant. Our data also show that there were periodic releases of carbon black from the plant in all years of study. It is, however, difficult to draw a definite conclusion about the reduction of plant

emissions over 4 years from these data because the downwind samples were collected at different distances from the plant in each sampling year. Dispersion modelling using this data set would be very useful in making these type of interpretations in future work. In addition, the carbon black method could be made faster, with lower sample turnaround times through the use of accelerated solvent extraction (ASE, also known as pressurized fluid extraction - PFE), silica Sep-Pak clean-up and analysis using fast GC-MS methods.

Our source samples also served in the development of a carbon black threshold based on the levels of thiacoronene and the total concentration of PAC in sample extracts. This threshold has become a tool in the identification of carbon black impacts in ambient air particulate. As this source apportionment research continues and other potential source samples become available for analysis, this statistical analysis yielding the carbon black threshold will also continue. With the collection and analysis of more air particulate samples and source samples in years to come, the carbon black threshold may change and perhaps become lower as the statistical sample size increases.

With the success of a source apportionment method based on organic chemical signatures, we decided to evaluate the use of PAC and metals in the source apportionment of black fallout in ambient air. Our carbon black source apportionment study showed that the majority of the "black fallout" in the east-end of Hamilton was derived from sources of pollution other than carbon black. This conclusion was based on the analysis of residential dust samples of black fallout and ambient air particulate collected downwind of the carbon black plant. Potential sources of black particulate (other than carbon black)

include steel industry-derived particulates from coking ovens, blast furnaces, rolling mills and fugitive emissions from outdoor coal, coke, slag piles and road dusts. There could also be potential contributions from vehicular emissions and smaller industries. We developed a new source apportionment strategy for steel industry-derived air particulate using metals. A new source apportionment tracer based on the levels of manganese and tin (two metals which are known releases by the steel industry) was proposed. The Mn-Sn metal index was used to differentiate different levels of steel industry impacts in ambient air. The use of the Mn-Sn metal index was compared versus an organic source tracer (the 234 Da thia-arene ratio) for the source apportionment of steel industry emissions.

Our preliminary evaluation of the use of metals versus PAC and thia-arene data in source apportionment has shown that the metal index has achieved equivalent efficacy in the identification of steel industry emissions. Overall, the Mn-Sn metal index has been found to be a valuable tool in differentiating air samples with minimal pollution impacts, and those having heavy steel industry impacts or mixed source contributions. We encourage further research in the use of the Mn-Sn index as a source apportionment tool, and a potential screening tool for steel industry impacts in ambient air samples. Future use of this metal source apportionment tracer has many potential advantages over organic source tracers, including lower analytical costs and faster sample turnaround times.

With respect to the "black fall-out" issue, the Mn-Sn metal index and the R234 thia-arene ratio were used in combination to evaluate the sources of ambient air

particulate in the east-end of Hamilton. The air particulate collected downwind of the steel industry coke ovens in 1996 were identified as having intermediate-to-heavy impacts from the steel industries. The heavy impacts were identified as having Mn-Sn metal index values above 1 (indicative of steel industry impacts) and R234 ratios below 3.1 (indicative of coke oven impacts). Five samples collected in the 1997/1998 air monitoring campaigns also were designated as having heavy steel industry impacts. Of the remaining samples from the 1997/1998 air monitoring campaigns, half were identified as having minimal (i.e., insignificant) steel industry impacts, and half were identified as having mixed source contributions. These air samples with mixed source contributions had Mn-Sn index values above 1 (indicating steel industry impacts), but also R234 ratios above 3.1 (indicative of combustion of petrogenic fuels or diesel emissions). This classification of mixed source impacts is highly plausible in an area that is surrounded by steel industry processes, truck and vehicular traffic and other industrial processes. There is great potential for re-entrainment of dusts from all of these particulate sources.

When the air samples that had been identified as having carbon black impacts were subjected to the metal index classification, the carbon black impacted samples exhibited impacts over the entire spectrum, from minimal (or insignificant) steel industry impacts to mixed source contributions to heavy steel industry impacts. The sample having the largest carbon black impact (i.e., July 6, 1998 – 1.12 μg carbon black/m^3) was classified as having mixed source contributions using this two-dimensional source apportionment method.

There are sources other than carbon black which are contributing to "black fallout." Our source apportionment method has shown that sources related to the steel industry, including coking operations, as well as combustion of petrogenic fuels (e.g., diesel emissions and other industrial combustion processes) are contributing factors to the black fallout problem in the City of Hamilton.

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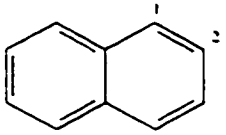
9. APPENDIX

Appendix I: STRUCTURES OF PAC

No.	Compound	Molecular Weight
2	Naphthalene	128
3	2-methylnaphthalene	142
4	1-methylnaphthalene	142
5	Biphenyl	154
6	Acenaphthylene	152
7	Acenaphthene	153
8	Fluorene	166
9	Dibenzothiophene	184
11	Phenanthrene	178
12	Anthracene	178
13	o-Terphenyl	230
15	Anthraquinone	208
16	Fluoranthene	202
17	Pyrene	202
19	m-Terphenyl	230
20	p-Terphenyl	230
21	Benzo[a]fluorene	216
22	Benzo[b]fluorene	216
23	Benzo[b]naphtho[2,1-d]thiophene	234
24	Benzo[ghi]fluoranthene	226
25	Benzo[c]phenanthrene	228
26	Benzo[b]naphtho[2,3-d]thiophene	234
27	Benz[a]anthracene	228
28	Cyclopenta[cd]pyrene	226
30	Chrysene	228
32	Benzanthrone	230
33	2-Nitrofluoranthene	247
34	Benz[a]anthracene-7,12-dione	258
37	Benzo[b]fluoranthene	252
38	Benzo[k]fluoranthene	252
39	Benzo[j]fluoranthene	252
40	Benzo[e]pyrene	252
41	Benzo[a]pyrene	252
42	Perylene	252
44	Indeno[1,2,3-cd]pyrene	276
45	Dibenz[ac]anthracene	278
46	Dibenz[ah]anthracene	278
47	Picene	278
48	Benzo[ghi]perylene	276
49	Coronene	300
53	Thiacoronene	306
54	Phenanthro[4,5-bcd]thiophene	208



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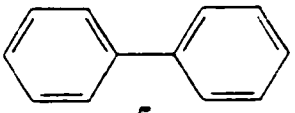

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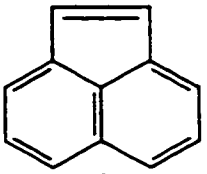

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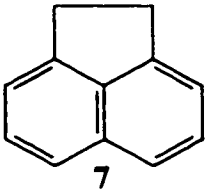

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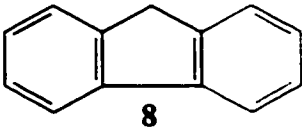

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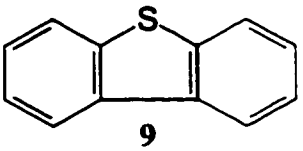

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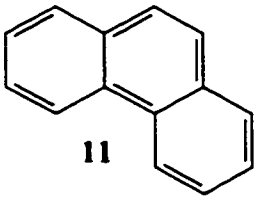

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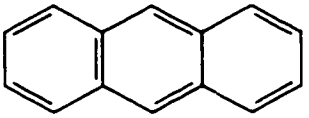

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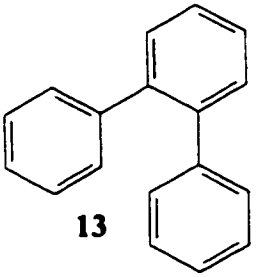

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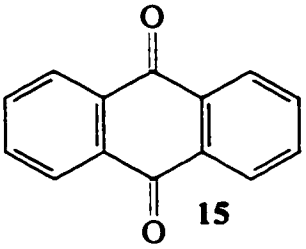

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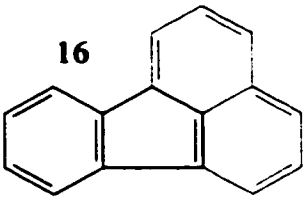

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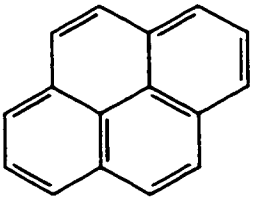

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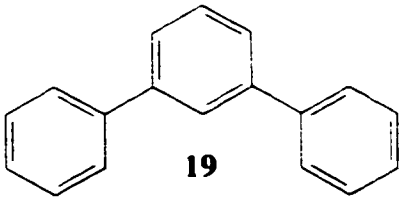

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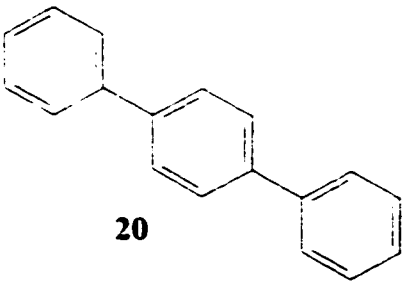

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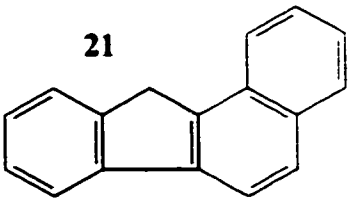

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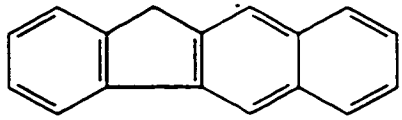

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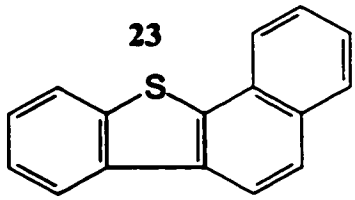

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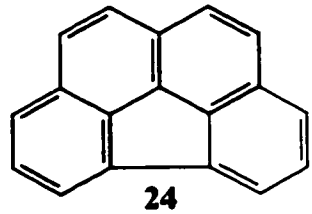

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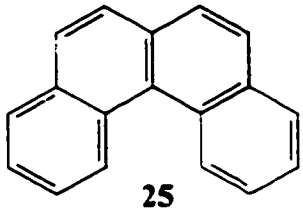

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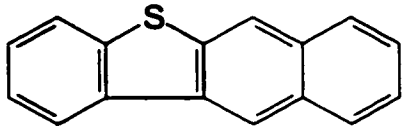

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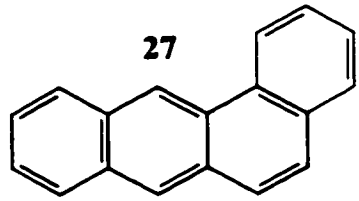

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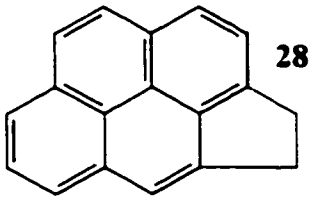

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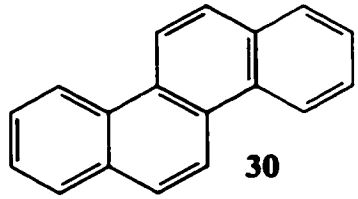

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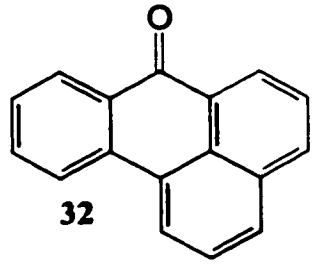

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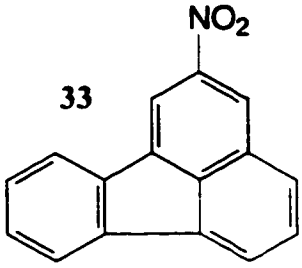

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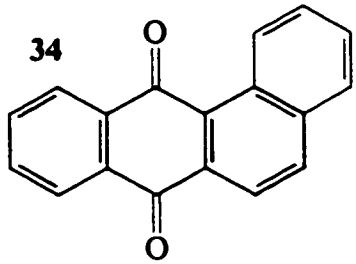

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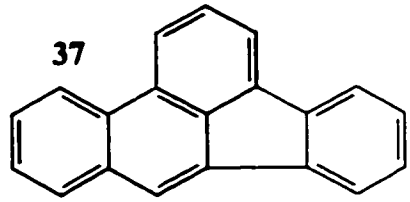

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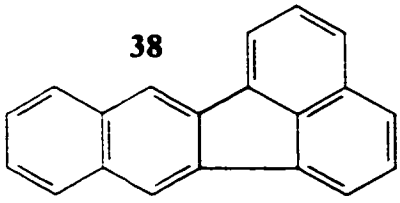

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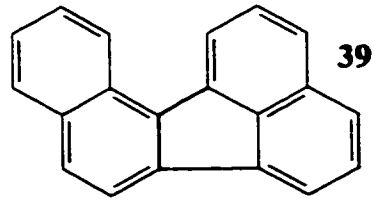

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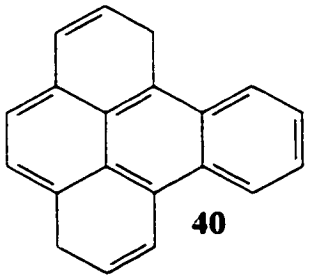

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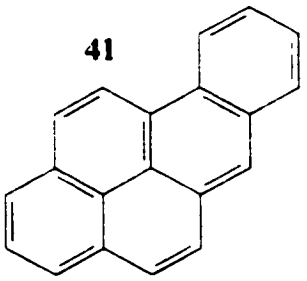

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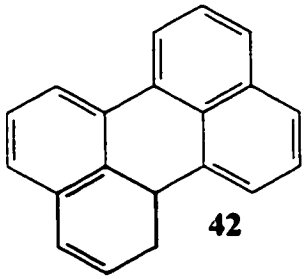

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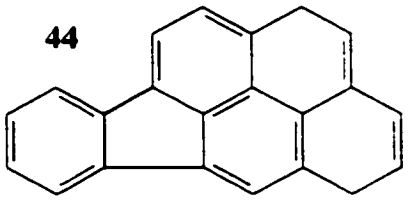

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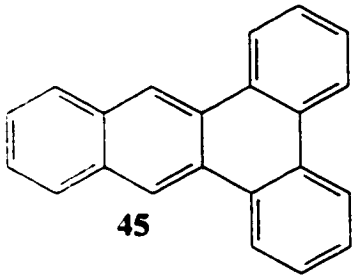

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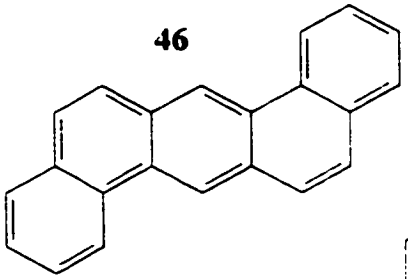

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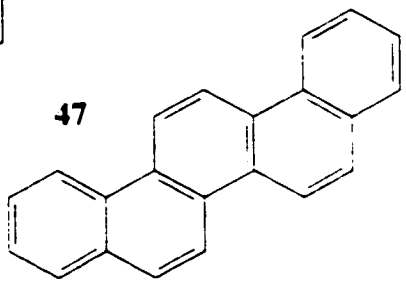

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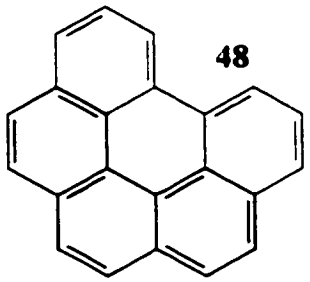

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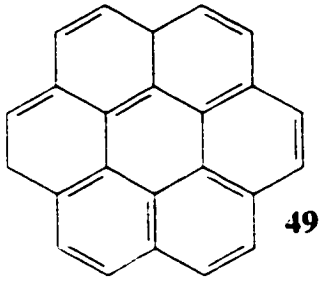

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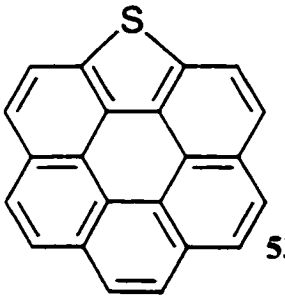

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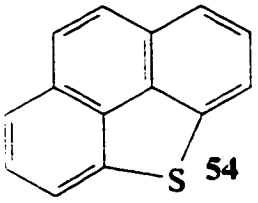

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Appendix II: INDUSTRIAL SOURCE SAMPLES

The source sample chart below gives a listing of the sample names and sample types (industrial/environmental origin), along with a detailed description of each sample's origin. Those samples which are of particular concern for air pollution have been denoted with an asterisk.

Each sample name has been given a two-letter prefix in order to identify its origin:

CC - Columbian Chemicals Canada Ltd.
DO - Dofasco Inc.
ST - Stelco Inc.
MO - Ministry of the Environment (Ontario)

INDUSTRIAL/ENVIRONMENTAL SOURCE SAMPLES

SAMPLE NAME	SAMPLE DESCRIPTION
CC-N550*	Carbon black derived from oil refinery bottoms; rubber grade for use in the carcasses of tires
CC-N330*	Carbon black derived from oil refinery bottoms; rubber grade for use in the tread of tires
CC-C1150*	Carbon black derived from coal tar combustion/tar pitch; used in electrical cables
DO-Pin*	Coal type: Pinacle #2 coal handling (black/granular)
DO-Kop*	Coal type: Kopperston (black/granular)
DO-Mas*	Coal type: Massey (black/granular)
DO-Egu*	Coal type: East Gulf (black/granular)
DO-PEM*	Pushing emissions control: Baghouse dust (black-metallic/sand)
DO-CBA *	Coal breeze A: derived from dryer baghouse (dark grey/powder)

DO-CBB *	Coal breeze B: derived from storage pile (grey-metallic/large granules)
DO-Mif*	Millscale fines: derived from storage pile (black/small granules)
DO-Sfn	Slag fines: derived from steel making (brown/sand)
DO-Bfs	Blast furnace slag: Pelletized (4BF) (grey/gravel and sand)
DO-Prs	Pit runner slag (4BF) (grey/2 large rocks)
DO-Sfb*	Slag fibres: from pelletizing operation
DO-4BF*	Baghouse dust from #4 blast furnace (brown/powder)
DO-Ksl	Kish sludge: derived from the Dekish station (grey and brown/granular)
DO-DES*	Baghouse dust derived from the Desulfurization station (grey/powder)
DO-HMT*	Baghouse dust: Kish oxide derived from Hot Metal Transfer
DO-LMb*	Baghouse dust: derived from the Ladle Metallurgy facility (brown/powder)
DO-Bol	Bottom lime: pulverized lime derived from the bottom injection system (white/powder)
DO-ARP	Oxide derived from the acid regeneration plant: sold for magnetic tape production (grey-metallic/small spheres)
DO- Cot	Coal tar: derived from #2 byproduct plant
DO-D1	Road dust - North perimeter Rd. - Heckett Dofasco
DO-D2	Road dust - West Perimeter Rd. - Next to west bayfront sewer
DO-D3	Road dust - Rd. North of boiler - #2 dock
DO-D4	Road dust - Blast Furnace - Rd. A
DO-D5	Road dust - Kenilworth Ave. - Coil storage south of 3 + 5 shear line
DO-D6	Road dust - Rd. southwest of east side filter
DO-D7	Road dust - Rd. between #6 and Sinter plant
DO-D8	Road dust - Rd. south of coal field - east-end
DO-D9	Road dust - Rd. west of BOF
ST-coc	coke oven condensate
ST-DA*	Docks - Blast Fce filter cake - #2 Dock
ST-DB*	Docks - Blast Fce flue dust - #2 Dock
ST-CQ	Coke Oven - Quench Station deposits
ST-DC*	Docks - Pelletized BF Slag screening fines - #3 Dock
ST-DD	Docks - East Side Lagoon sludge - #3 Dock
ST-DE*	Docks - #3 Dock sunken vessels dust deposits

ST-SP*	Steelmaking - BOF - Precipitator Dust
ST-SB*	Steelmaking - BOF -"B" Baghouse Dust
ST-SM*	Steelmaking - BOF - Multiclone Dust
ST-HS*	Heckett's - Screening operation fines
ST-SS*	Sinter Plant - Fine sinter dust deposits
ST-BF*	Blast Fce - Casthouse baghouse dust
ST-CT*	Coke Oven - Top side dust

MOE Street Dusts	
MO-SDF	on Industrial Dr.-Burlington St. - South of Dofasco
MO-WST	on Burlington St. West of Stelco between Wellington and Wentworth
MO-SCC	on Burlington St. South of Columbian
MO-WCC	on South Gateway - due West of Columbian
MO-NDS	on Beach Blvd. NE of Dofasco/Stelco
MO-SST	on Burlington St. - Industrial Dr. South of Stelco
MO-PHL	Philip Site near Columbian

STANDARD REFERENCE MATERIALS	SAMPLE DESCRIPTION
SRM 1649	Urban Air Reference Sample (dark grey dust)
SRM 1650	Diesel Particulate Reference Sample

Appendix III: EXPERIMENTAL

A. INSTRUMENTATION

GC/MS Analysis

Gas chromatographic analyses were performed using a Hewlett-Packard Model 5890 Series II Gas Chromatograph equipped with a DB-17ht capillary column (30 m. x 0.25 mm i.d. x 0.15 μm film, J & W Scientific, Folson, CA) and an on-column injector. The detector consisted of a Hewlett-Packard Model 5971A Mass Selective Detector. For the most part, samples were analysed in selected ion monitoring mode; some samples were run in full scan mode in order to detect non-target components. Internal standards (pyrene-d_{10} and perylene-d_{12} or dibenz[a,h]anthracene-d_{14}) were added to samples prior to analysis. The GC-MS temperature program was as follows: injection at 90°C, program from 90-300°C at 2.5 °C /min. then held at 300°C for 20 min.

The preparation of the samples for GC-MS analysis varied somewhat depending on sample type. Variables such as sample type and extract colour aided in the determination of how much of the sample would be prepared for analysis and injected onto the column. The sample preparation method is determined at the discretion of the analyst, a result of his/her experience in sample analysis by GC-MS. In some cases, a known volume of internal standard was added to the sample vial, and then an accurate aliquot of that volume was then transferred to a 1.5 mL GC autosampler vial, equipped

with a 100 uL insert, for GC-MS analysis. In other cases a portion of the sample extract was aliquotted for GC-MS analysis by adding a known volume of dichloromethane to the sample extract residue in the vial (e.g., 100 uL dichloromethane via 100 uL syringe), mixing via quick vortexing and transfer of a known volume of the extract to a 1.5 mL GC autosampler vial fitted with a 100 uL inner sample tube (e.g., 50 uL transferred, representing 50 % of the sample extract). For greater accuracy in the extract spike experiment, the entire extract was transferred to a volumetric flask (e.g., a 1 mL volumetric flask), and a known volume was transferred to a GC-MS vial. In every case, a known volume of internal standard in toluene solution was added to the GC-MS sample prior to analysis.

The GC-MS conditions used for sample extract analysis are listed in Table A.3.1. A selected ion monitoring program was developed to monitor the ions listed in Table A.3.2. The large number of ions monitored allowed the detection of many compounds and the confirmation of compound identity through the detection of characteristic fragment ions.

Table A.3.1 Instrumental parameters used for GC-MS analysis

PARAMETER	CONDITIONS
Stationary Phase	DB-17ht
Column Length	30 m
Column I.D. (mm)	0.25 microns
Film Thickness	0.15 microns
Oven Temperature Program:	
Initial Temp. (°C)	90
Rate (°C/min)	2.5
Final Temp. (°C)	300
Final Time (min)	20
Injector	Cool on-column
Detector Temp. (°C)	300
Carrier Gas	He
Flow Rate (mL/min)	1.0

Table A.3.2 Selected Ion Monitoring program used in GC-MS analyses

GROUP #	START TIME (min)	IONS MONITORED
1	5.0	128, 129, 136, 139, 141, 142, 151, 152, 153, 154, 162, 165, 166, 176, 178, 179, 184, 188, 189, 191
2	35.5	139, 152, 180, 184, 191, 192, 197, 198, 202, 203, 205, 206, 208, 211, 212, 219, 220, 225, 226, 229, 230
3	43.0	163, 191, 202, 203, 205, 206, 208, 212, 213, 215, 216, 219, 220, 221, 222, 225, 226, 229, 230, 231, 234
4	50.5	117, 189, 202, 215, 216, 221, 222, 226, 227, 228, 229, 230, 234, 235, 236, 240, 243, 244
5	56.5	117, 189, 202, 226, 227, 228, 229, 230, 234, 235, 236, 239, 240, 241, 242, 243, 244, 247, 248, 255, 256
6	59.5	117, 189, 201, 202, 217, 228, 230, 234, 239, 240, 241, 242, 243, 244, 247, 248, 255, 256, 261, 262, 275, 276
7	61.5	189, 201, 217, 230, 234, 239, 240, 241, 242, 244, 247, 248, 253, 254, 255, 256, 258, 261, 262, 269, 270, 275, 276
8	63.5	201, 213, 217, 230, 234, 239, 240, 241, 242, 247, 252, 253, 254, 255, 256, 258, 261, 262, 267, 269, 270, 275, 276
9	65.5	213, 252, 253, 254, 255, 256, 258, 261, 262, 264, 265, 266, 267, 268, 269, 270, 271, 272, 275, 276
10	70.3	213, 252, 253, 254, 258, 260, 264, 265, 266, 267, 268, 269, 270, 271, 272, 275, 276, 280, 285, 286
11	71.0	213, 239, 252, 253, 258, 260, 264, 265, 266, 268, 269, 270, 271, 272, 275, 276, 278, 279, 280, 284, 285, 286, 299, 300
12	73.0	213, 239, 252, 258, 265, 266, 268, 269, 270, 271, 272, 275, 276, 278, 279, 280, 282, 284, 285, 286, 293, 294, 299, 300
13	76.5	239, 271, 272, 276, 277, 278, 279, 280, 282, 284, 285, 286, 288, 289, 290, 292, 293, 294, 299, 300, 303, 304
14	79.8	239, 261, 271, 272, 276, 277, 278, 279, 280, 282, 284, 285, 286, 289, 290, 292, 293, 294, 299, 300, 303, 304, 306
15	82.3	150, 239, 261, 276, 277, 278, 282, 284, 285, 286, 289, 290, 292, 293, 294, 299, 300, 302, 303, 304, 306, 317, 318

HPLC Analysis

Reversed and normal phase HPLC were performed on a Hewlett-Packard Model 1090 liquid chromatograph equipped with a built-in diode array detector. HPLC operating conditions were as follows: diode array detection over the wavelength range from 250 - 370 nm; column temperature, 40°C.

Semi-preparative normal phase chromatography was performed using an amino precolumn (Brownlee Labs, Santa Clara, CA, 1.5 cm x 3.2 mm i.d.) and a 10 micron Whatman Partisil M9 PAC semi-preparative column (Whatman, Clifton, NJ, 25 cm x 9.4 mm i.d.). A hexane/dichloromethane (hex./DCM) gradient elution program was used (elapsed time, composition of mobile phase): initial, 95% hex. and 5% DCM; 35 min., 70% hex. and 30% DCM; 55 min., 30% hex. and 70% DCM; 65 min., 100% DCM; 70 min., 95% hex. and 5% DCM; flow rate: 4.2 mL/min.

Analytical reversed phase chromatography was performed using a 5 micron 25 cm x 4.6 mm i.d. Vydac 201TP54 reversed phase column (Separations Group, Hesperia, CA.). A water/acetonitrile gradient elution program was used (elapsed time, composition of mobile phase): initial, 40% water and 60% acetonitrile; 25 min., 100% acetonitrile; 35 min, 80% acetonitrile and 20% dichloromethane; 37 min., 100% acetonitrile; 40 min, 40% water and 60% acetonitrile; flow rate: 1.0 mL/min.

UV-Vis and Fluorescence Analyses

UV-Vis analyses were performed using a Perkin-Elmer, Model Lambda 9, UV/VIS/NIR spectrophotometer equipped with a Perkin-Elmer printer/plotter. Fluorescence analyses were performed on a Perkin-Elmer, Model LS-5 spectrofluorimeter.

Probe Mass Spectral Analysis

A sample isolated during HPLC peak fractionation was analysed in the McMaster Regional Centre for Mass Spectrometry. The analysis was performed by direct inlet probe analysis with electron impact ionization (electron energy 70 eV) at low resolution or at high resolution (HR-MS) for precise molecular weight determination. Analyses were performed using a VG ZAB-E mass spectrometer (VG Analytical, Altrincham, U.K.). A PDP 11/24 data system (Digital Equipment Co.) was used for data acquisition and analysis.

Inductively-Coupled Plasma Mass Spectrometry (ICP/MS)

ICP/MS analysis (excluding sample preparation) was contracted out to a commercial laboratory (Activation Laboratories Ltd., Jerseyville, Ontario). Sample preparations including sample grinding and preparation of filters were performed at McMaster. Air filters were stamped with a die (3.3 cm in diameter, filter area 8.55 cm^2) in the middle of the filter in efforts to ensure filter portions for analysis were representatively similar. The stamped filter disks represented approximately 2.02 % of the total sampling area on the air filters (23.5cm x 18cm total sampling area: approximately 423 cm^2). Samples were digested in a solution of nitric acid and hydrogen peroxide at Activation Labs prior to analysis by ICP-MS.

X-ray Crystallography

X-ray crystallographic data were collected by Dr. J. Britten from a single crystal of thiacoronene which was mounted by Dr. R. Ruffolo on a glass fibre and transferred to a P4 Siemens diffractometer, equipped with a rotating anode and graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Three standard reflections, that were measured after every 97 reflections, showed neither instrument instability nor crystal decay. Data were corrected for absorption using an empirical ψ-scan method. The structure was solved by Dr. R. Ruffolo by using the direct methods procedure in the Siemens SHELXTL program library[160], and refined by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms.

B. SAMPLE PREPARATION FOR PAC ANALYSIS BY GC-MS

B.1 PRINCIPLE OF METHOD

The samples were extracted using a Soxhlet apparatus, then cleaned by two-stage adsorption chromatography to remove organic interferences. All samples (air samples and source samples) were extracted using a Soxhlet apparatus with dichloromethane for 24 hours to afford a dichloromethane extract, followed by a second extraction with toluene for 24 hours to afford a second toluene extract. The two extracts were cleaned up and analyzed separately. A non-polar aromatic fraction was prepared using a silica Sep-Pak Cartridge followed by Sephadex LH20 chromatography. The sample extracts are

subjected to quantitative GC-MS analysis using selected ion monitoring (SIM) data acquisition mode.

Parameters Measured

The target PAC evaluated are listed in Table 4.8. The term "Total PAC" is used in the present research to define the sum of the concentrations of all target native PAC detected in each sample. The target PAC list contains only a subset of all known native PAC compounds; hence, this fact should be considered when comparing the Total PAC values determined in this research to other "Totals" values reported elsewhere.

Sample Handling

Great care is required in order to ensure that samples are not contaminated during sample handling, preparation or storage. Air filters were stored in their envelopes and placed in a sealed bag (e.g., a zip-lock bag) in a freezer (-20 degrees Celsius). Other particulate samples were stored in glass jars or vials with caps lined with aluminum foil or Teflon in order to prevent sample contamination with plasticizers. All sample extracts were stored in glass vessels capped with aluminum foil or Teflon. All vial caps were lined with aluminum foil or Teflon. Under no circumstances were sample extracts allowed to come in contact with anything other that solvent-rinsed (glass-distilled solvent only) glassware, solvent-rinsed glass wool and extraction supplies (e.g., pre-extracted cellulose thimbles or solvent-rinsed quartz boiling granules) and aluminum foil or Teflon.

Standards and Chemicals

High purity helium carrier gas (>99.9 %) was purchased from VitalAir (Hamilton, Ontario). HPLC grade solvents were purchased from Caledon Laboratories (Georgetown, Ontario) and Aldrich Chemicals Company Inc. (Milwaukee, WI). A Milli-Q purification system (Waters Associates, Millford, Massachusetts) was used to further purify distilled water.

PAH standards were purchased from Aldrich Chemical Company Inc. (Milwaukee, WI). Thiacoronene was isolated during the present research from extracts of carbon black using high-performance liquid chromatographic fractionation in normal phase. Deuterated PAH standards were purchased from Cambridge Isotope Labs Ltd. (Woburn, MA).

The following standards mixtures were prepared for the present research:

Spike Recovery Standard (in dichloromethane)

phenanthrene-d_{10}	(0.732 µg/mL)
chrysene-d_{12}	(0.852 µg/mL)
dibenz[a,h]anthracene-d_{14}	(0.820 µg/mL)

Internal Standard (in toluene)

pyrene-d_{10}	(4.998 µg/mL)
perylene-d_{12}	(4.008 µg/mL)

Table A.3.3: Thiacoronene Standards (in toluene)

Thiacoronene Standard	Thiacoronene (μg/mL)	Perylene-d_{12} (μg/mL)
CAL3061	5.53	10.02
CAL3062	1.45	2.51
CAL3063	0.60	1.00
CAL3064	0.31	0.50
CAL3065	0.16	0.25
CAL3066	0.033	0.050
CAL3067	0.006	0.010

Calibration Standard

A calibration standard containing 45 polycyclic aromatic compounds and 5 deuterated PAH was prepared for compound identification; the 50 compounds are listed in Table A.3.4 (thiacoronene was not included in the calibration standard but was included in the PAC target list for quantification). Peak numbers are listed which identify each compound in the standard along with the concentration of each compound. An example chromatogram of the calibration standard is shown in Figure A.3.1 which includes the peak identifications. Native PAC with peak numbers 2 to 30 were quantified using pyrene-d_{10} as the internal standard. Native PAC peak numbers 32 to 53 were quantified using perylene-d_{12} as the internal standard. An individual standard of native thiacoronene (CAL3065) was used for the identification of thiacoronene in samples.

Table A.3.4: Concentrations of PAC in GC-MS calibration standard CSTDA7

Peak No.	Compound Name	Mass (g/mol)	Conc. (µg/mL)
2	Naphthalene	128	0.840
3	2-Methylnaphthalene	142	0.780
4	1-Methylnaphthalene	142	0.702
5	Biphenyl	154	0.986
6	Acenaphthylene	152	0.816
7	Acenaphthene	154	0.846
8	Fluorene	166	0.846
9	Dibenzothiophene	184	1.208
11	Phenanthrene	178	1.600
12	Anthracene	178	1.964
13	o-Terphenyl	230	0.830
14	1-Methylphenanthrene	192	0.862
15	Anthraquinone	208	1.968
16	Fluoranthene	202	1.368
17	Pyrene	202	1.470
18	9,10-Dimethylanthracene	206	0.798
19	m-Terphenyl	230	0.836
20	p-Terphenyl	230	0.834
21	Benzo[a]fluorene	216	0.848
22	Benzo[b]fluorene	216	0.892
23	Benzo[b]naphtho[2,1-d]thiophene	234	0.442
24	Benzo[ghi]fluoranthene	226	1.322
25	Benzo[c]phenanthrene	228	0.842
26	Benzo[b]naphtho[2,3-d]thiophene	234	0.906
27	Benz[a]anthracene	228	1.380
28	Cyclopenta[cd]pyrene	226	0.960
30	Chrysene	228	1.520
32	Benzanthrone	230	1.800
33	2-Nitrofluoranthene	247	1.130
34	Benz[a]anthracene-7,12-dione	258	1.846
35	1-Nitropyrene	247	1.438
36	2-Nitropyrene	247	1.450
37	Benzo[b]fluoranthene	252	1.294
38	Benzo[k]fluoranthene	252	0.950

39	Benzo[j]fluoranthene	252	0.930
40	Benzo[e]pyrene	252	1.382
41	Benzo[a]pyrene	252	1.054
42	Perylene	252	1.198
43	3-Methylcholanthrene	268	0.958
44	Indeno[1,2,3-cd]pyrene	276	1.286
45	Dibenz[a,c]anthracene	278	1.490
47	Picene	278	1.058
48	Benzo[ghi]perylene	276	1.266
49	Coronene	300	0.858
50	Dibenzo[a,e]pyrene	302	0.884
51	Dibenzo[a,i]pyrene	302	0.904
52	Dibenzo[a,h]pyrene	302	1.018
53	Thiacoronene	306	individual std.
1	d10-pyrene	212	1.000
10	d10-phenanthrene	188	0.732
29	d12-chrysene	240	0.852
31	d12-perylene	264	0.802
46	d14-dibenz[a,h]anthracene	292	0.820

Chromatographic resolution in the GC-MS analysis was assessed by evaluation of the peak resolution for the 252 Da benzofluoranthene isomers. The criterion that was required to be met prior to PAC analysis of samples was a peak resolution between benzo[b]fluoranthene and benzo[k]fluoranthene yielding a valley of less than 30% of the peak height of benzo[b]fluoranthene. In order to assess instrumental response at low concentration, a low-level thiacoronene standard was analysed (CAL3066; 50 pg injected) at a level approximately 10X the compound detection limit.

Figure A.3.1: GC-MS total ion chromatogram (SIM mode) of the calibration standard CSTDA7 (chromatogram is given over 2 pages).

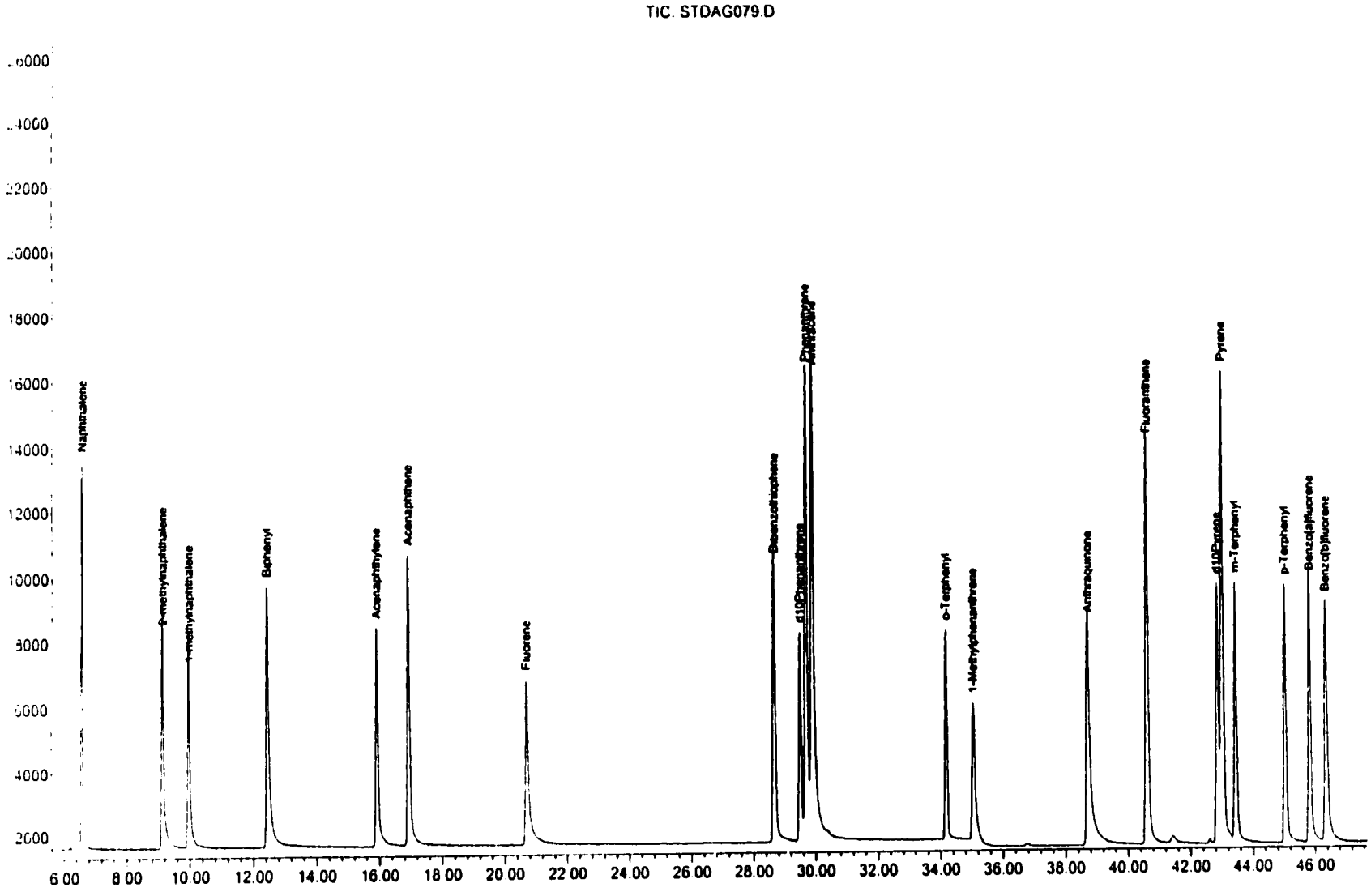
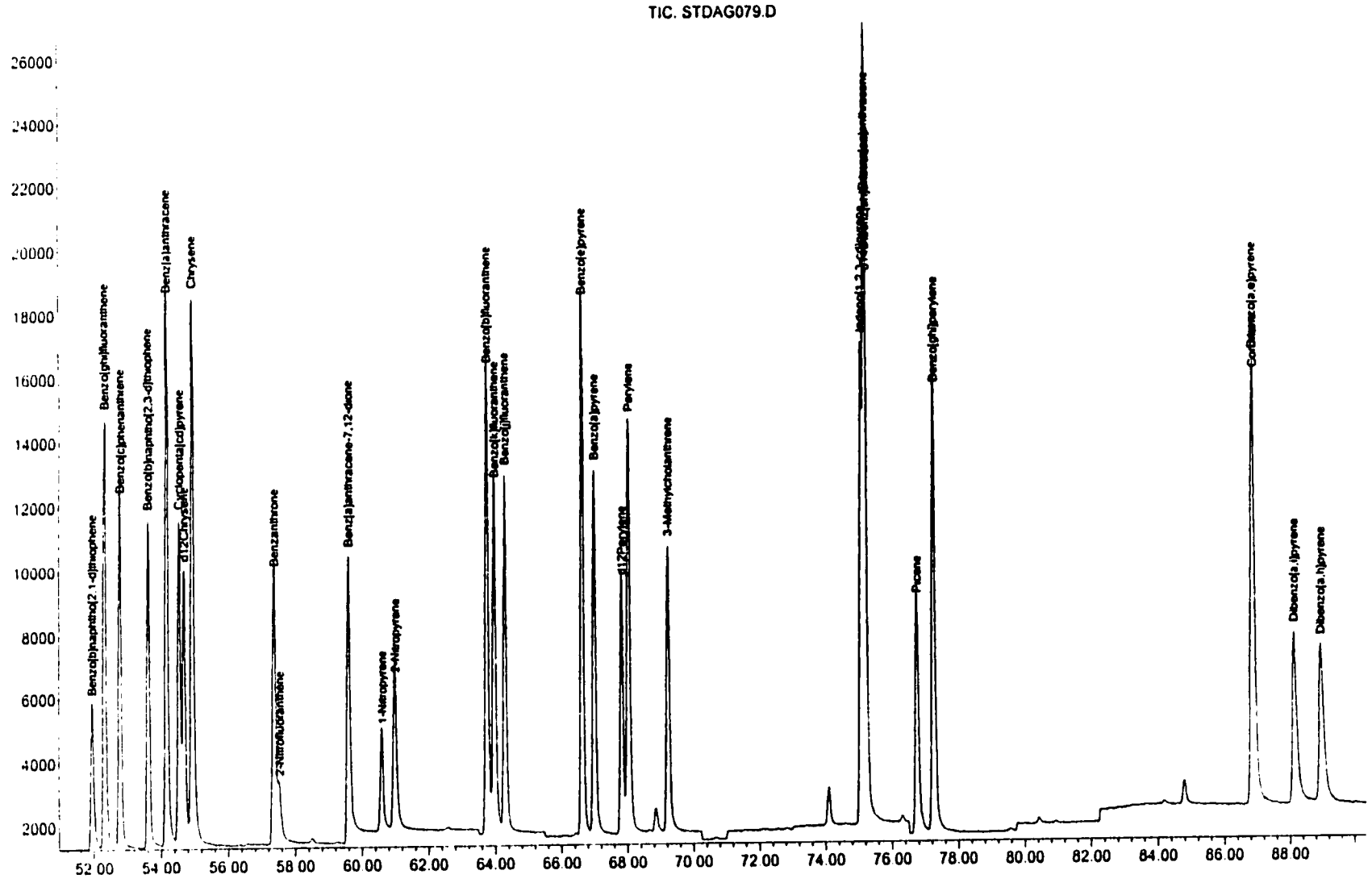


Figure A.3.1: GC-MS total ion chromatogram (SIM mode) of the calibration standard CSTDA7 (chromatogram is given over 2 pages).



B.2 SOXHLET EXTRACTION

All solvents used for extraction or solvent rinsing must be of glass-distilled grade or HPLC grade or suitable for pesticide residue analysis. All glassware and labwares in direct contact with samples were scrubbed with scrub brushes, washed with water and laboratory detergent (Sparkleen; Fisher Scientific) rinsed 7-10 times with distilled water, dried, and pre-rinsed 3-4 times with glass-distilled dichloromethane. Syringes were rinsed 10-15 times with dichloromethane before use and between uses. Cellulose Soxhlet thimbles were pre-extracted with glass-distilled dichloromethane for at least 6 hours and air-dried before use. Soxhlet extraction apparatus used for sample extractions were approximately 80 mL volume while the Soxhlet apparatus used for pre-extraction of thimbles was much larger and could accommodate 8 thimbles at once.

In the Soxhlet extraction procedure, 3-5 quartz boiling granules were placed into a 250 mL round bottom flask filled with approximately 180 mL of dichloromethane. The sample was placed in the Soxhlet extraction apparatus (Kimax Soxhlet with fitted condenser) and fortified with 500 µL of the spike recovery standard using a 500 µL syringe. Air filters were folded in half lengthwise and then rolled before being placed in the Soxhlet using clean long tweezers. Solid particulate samples were weighed into a tared pre-extracted cellulose thimble using an analytical balance. Once the sample was in the cellulose thimble, the sample was covered by a loose plug of solvent-rinsed glass wool in order to prevent loss of particulate material. Condensing solvent in the soxhlet

was made to drip directly into the thimble to ensure intimate contact between the hot solvent and the sample.

The Soxhlet apparatus was assembled and the heat setting was adjusted depending on the solvent used for extraction: "medium" heat level for dichloromethane and "high" heat for toluene or chlorobenzene (heating mantle - Sargent-Welch Scientific Co., Skokie Illinois, catalog # S41315). Samples were extracted for 24 hours at a rate of 4-7 cycles per hour. Cycling rates were recorded for each extraction setup. Flasks and the lower part of the Soxhlet unit including the "J-tube" were wrapped with aluminum foil; this was especially necessary with high-boiling solvents such as toluene and chlorobenzene. Seals between glass joints were checked to ensure a tight fit to prevent loss of solvent from the apparatus. If the solvent did not cycle, the entire Soxhlet unit was carefully angled and rotated to force the Soxhlet to drain. Soxhlets were adjusted until cycling occurred naturally without force.

After extraction, the Soxhlet units were allowed to cool and any residual solvent was siphoned into the round bottom flask (the Soxhlet unit can be tipped slightly to create a siphon). If the sample was to be extracted with a second solvent, the Soxhet apparatus was disassembled and the upper part containing the extracted sample was placed in the fumehood for approximately 24 hours to ensure the sample was dry. For the second solvent extraction, the dried sample was re-extracted with the second solvent (normally toluene) in the same manner as described above except that a new round bottom flask and fresh solvent was used. No spike recovery standard was added to the second extraction.

The solvent extract was evaporated at reduced pressure using a rotary evaporator to a volume of approximately 1-2 mL. Water bath temperatures were approximately 30 °C for dichloromethane, and approx. 55 °C for toluene and chlorobenzene. Toluene and chlorobenzene extracts were reduced in volume to achieve "just dryness" and then 2-3 mL of dichloromethane was added to the extract residue as a "keeper solvent". All samples were stored refrigerated in the dark.

B.3 SILICA SEP-PAK CLEAN-UP OF SAMPLE EXTRACTS

The Sep-Pak clean-up procedure was based on standard methods used by the MOE and Environment Canada for the clean-up of extracts targeted for PAH analysis. A silica Sep-Pak cartridge (Waters Corporation, Milford MA) attached to a 5 mL Luer-lok syringe reservoir (Becton Dickinson) was clamped vertically above a beaker or Erlenmeyer flask. The reservoir/cartridge was flushed with 7mL of dichloromethane dispensed from a glass disposable pipette. The dichloromethane wash was collected and discarded. A 50 mL roundbottom flask was placed under the cartridge. Without allowing the washed Sep-Pak to dry out, a sample extract in dichloromethane solution was quantitatively transferred to the Sep-Pak using a clean disposable glass pipette. The 250 mL roundbottom which contained the sample was washed 4-5 times with dichloromethane (1 mL) and each washing was transferred to the syringe-Sep-Pak combination ensuring the Sep-Pak cartridge never became dry. [Note: sometimes an air lock in the bottom of the syringe reservoir causing the sample to flow very slowly; this air

lock could be removed by dispensing the sample directly into the Luer-lok portion of the syringe by placing the pipette as far down as it can go before dispensing] The silica cartridge was eluted with an additional 7 mL of dichloromethane and the eluate (approximately 15 mL) was collected in a 50 mL roundbottom flask. The eluted fraction was evaporated carefully to approximately 0.5 mL at reduced pressure using a warm water bath (approximately 30 degrees C for dichloromethane and approx. 55 degrees C for toluene and chlorobenzene).

This fraction (analogous to fraction A23 from other methods published by our group) was then quantitatively transferred to a 1 dram mini vial using a clean glass disposable pipette. The first transfer was then taken to near dryness using a Reacti-Vap blowdown apparatus (a slow stream of nitrogen with low heat or no heat at all). A rinse (approx. 0.25 mL dichloromethane) was added to the 50 mL roundbottom flask and the resulting solution was transferred to the same vial and blown down; the 0.25 mL rinse, transfer and blowdown sequence was repeated 4 times. All efforts were made to maintain the sample residue in the bottom of the vial to ensure a quantitative transfer to the Sephadex LH-20 Column.

B.4 SEPHADEX LH-20 CHROMATOGRAPHIC CLEAN-UP PROCEDURE

The Sephadex LH-20 procedure has been published by our lab group.[161] A Beckman Model 110A HPLC pump equipped with a Beckman Model 153 Analytical Ultraviolet Absorption Detector was used (Beckman Instruments, Fullerton, CA;

wavelength of detection 254 nm, flow cell pathlength 5 mm). Signal recording was performed using a strip chart recorder (Chart recorder setting: 2 mm/min). Two column sizes were used for the Sephadex LH-20 separation: column one: (4 cm x 30 cm glass column; flow rate 3 mL/min; 1 mL injection loop); column two: (0.94 cm x 10 cm stainless steel column- Niagara Valve and Fittings Ltd, Hamilton, Ont.; flow rate 0.4 mL/min; 250 μL injection loop).

The LH-20 mobile phase (hexane:methanol:dichloromethane, 6:4:3 by volume) was degassed before use by a helium sparge. Sephadex LH-20 gel was allowed to soak overnight in the mobile phase followed by degassing under vacuum. A portion of the slurry was poured into a column. The column was packed by pumping eluent through the column at 1.5 times the working flow rate (see above). If necessary, more slurry was added to the column and the column was repacked as described. After packing, the column was equilibrated by pumping mobile phase through the column at the working flow rate. The performance of the column packing was tested by injecting 250 μL of a 1 mg/mL solution of naphthalene dissolved in mobile phase. A symmetrical peak shape and a consistent elution time for 2-3 sequential injections indicated that the column was ready for use. The time and elution volume (as determined using a graduated cylinder) from injection until the start of the naphthalene peak were recorded.

The extract (having previously undergone silica Sep-Pak clean-up) was prepared for injection onto the Sephadex LH-20 chromatography column in the following manner: [this description is the procedure for a 250 μL loop injection]. Using a 500 μL syringe,

the instrument injection loop was first flushed with mobile phase. The sample was dissolved in 40 μL of dichloromethane followed by the addition of 160 μL of the mobile phase solvent. The 250 μL injection syringe was first flushed with mobile phase and pumped to remove air bubbles; the syringe was then filled to 30 μL with mobile phase. The partially filled syringe was then used (slowly and carefully) to draw the dissolved sample completely into the syringe, ensuring that no air bubbles enter the syringe. The sample (total approximate volume of 230 μL) was then slowly loaded into the 250 μL injection loop for on-column injection and injected (these injection volumes were scaled up appropriately for injections onto a 1 mL injection loop).

[Note: The purpose of partially filling the top portion of the syringe with 30 μL of mobile phase was to aid in the quantitative transfer of the sample to the chromatographic column. If the sample loading and injection steps are performed slowly and carefully, the first 30 μL in the top of the syringe will largely remain unmixed with the sample and will fill the "dead volume" in the injection port, ensuring that all of the sample is loaded onto the LH-20 column.]

Immediately upon injection, the chart recording was marked to record the start of the run and the column eluate was collected in a 10 mL graduated cylinder. Material eluting prior to naphthalene (consisting primarily of aliphatic materials) was collected and transferred to vials for storage (this fraction was referred to as the "A0" fraction). The

elution time of naphthalene was considered to begin at the time measured at the start of the naphthalene peak on the strip-chart recorder (after approximately 15 min. and 6 mL eluted). Once the elution time of the naphthalene standard had elapsed, the collection flask was changed to a 50 mL roundbottom flask in order to collect the non-polar aromatic fraction of the sample (analogous to sample fraction called A23LH-20 in previous publications from our lab group). The non-polar aromatic fraction of the sample extract was collected until the UV signal had returned to baseline.

The non-polar aromatic fraction in the 50 mL round bottom flask was evaporated under reduced pressure to approximately 0.5 mL at a warm water temperature (approximately 30 degrees C) and under vacuum supplied by a water tap aspirator. The sample was then quantitatively transferred to a 1 dram mini-vial, as described above. The samples were analysed using GC-MS as described previously.

C. RECOVERIES OF PAC FROM SRM1650

The PAC obtained from the SRM1650 extract were analyzed by GC-MS. PAC concentration ranges determined by the NIST were then compared to concentrations determined using this method; both sets of values appear in Table A.3.5. Concentrations determined using this method generally fell within the certified range reported by NIST. Since the PAC concentrations (on a μg/g basis) in diesel soot and air particulate are similar, these experiments have demonstrated that our methodology is applicable and appropriate to the analysis of PAC in air particulate.

Table A.3.5 Recoveries of PAC from SRM1650 (diesel soot)

Compound	Concentration Range (μg/g; as reported by NIST)	Concentration Range Determined by this Method*
Fluoranthene	51 ± 4 (certified)	51 ± 2
Pyrene	48 ± 4 (certified)	50 ± 2
Benz[a]anthracene	6.5 ± 1.1 (certified)	5.7 ± 0.2
Benzo[a]pyrene	1.2 ± 0.3 (certified)	1.3 ± 0.06
Benzo[ghi]perylene	2.4 ± 0.6 (certified)	7.8 ± 0.3
Phenanthrene	71 (non-certified)	50 ± 11
Benzo[e]pyrene	9.6 (non-certified)	13 ± 0.6
Indeno[cd]pyrene	2.3 (non-certified)	6.3 ± 0.3

* uncertainty in determined concentrations were derived from the uncertainty estimates for this method (see Section 4.7.1)

Appendix IV: Wind data and particulate concentrations for all air particulate filters collected for this study in Hamilton, 1995 - 1998

Appendix IV: Wind data and particulate (PM_{10}) concentrations for all air particulate filters collected for this study in Hamilton, 1995-1998

Filter #	Date	Average Wind Direction (std. dev.)	Average Wind Speed (km/hr)	# Hours Low Wind Speed - *1	Site - *2	Particulate Conc. (µg/m3)
1078	7/10/95	180 (96)	5.2	7	Philip	118
1079					Gertrude	47
1073	7/11/95	32 (64)	6.3	5	Philip	95
1074					Gertrude	70
1069	7/12/95	146 (80)	6.8	7	Philip	78
1067					Gertrude	62
1059	7/13/95	232 (52)	7.1	2	Philip	157
1058					Gertrude	60
1047	7/14/95	250 (33)	8.5	1	Philip	73
1053					Gertrude	44
1044	7/15/95	35 (93)	6.0	8	Philip	20
1045					Gertrude	12
none	7/16/95	51 (113)	3.7	7	Philip	n/a
1057					Gertrude	29
1369	7/17/95	246 (25)	7.7	2	Philip	85
1372					Gertrude	24
1357	7/18/95	272 (12)	11.7	1	Philip	157
1359					Gertrude	34
1362	7/19/95	254 (35)	6.7	6	Philip	96
1361					Gertrude	28
1245	7/20/95	238 (7)	10.4	0	Philip	125
1247					Gertrude	27
1368	7/21/95	101 (55)	6.5	7	Philip	139
1238					Gertrude	50
1233	7/22/95	147 (78)	4.5	7	Philip	57
1236					Gertrude	59
1228	7/23/95	265 (44)	8.0	5	Philip	38
1229					Gertrude	19
1032	7/24/95	74 (41)	2.7	12	Philip	52
1036					Gertrude	64
1027	7/25/95	132 (109)	4.8	4	Philip	85
1055					Gertrude	68
1023	7/26/95	283 (68)	3.6	12	Philip	75
1021					Gertrude	39
1189	7/27/95	71 (37)	6.4	10	Philip	66
none					Gertrude	n/a
1202	7/28/95	223 (55)	6.4	1	Philip	79
none					Gertrude	n/a
1214	7/29/95	264 (30)	7.0	6	Philip	51
1210					Gertrude	25
1194	7/30/95	123 (63)	5.6	10	Philip	37
1196					Gertrude	28
1150	7/31/95	176 (64)	6.3	5	Philip	110
1153					Gertrude	49

Appendix IV: Wind data and particulate (PM_{10}) concentrations for all air particulate filters collected for this study in Hamilton, 1995-1998

Filter #	Date	Average Wind Direction (std. dev.)	Average Wind Speed (km/hr)	# Hours Low Wind Speed - *1	Site - *2	Particulate Conc. (µg/m3)
1161	8/1/95	297 (61)	6.8	2	Philip	168
1158					Gertrude	66
1136	8/2/95	61 (12)	8.2	1	Philip	44
1138					Gertrude	80
1144	8/3/95	67 (109)	5.4	7	Philip	57
1146					Gertrude	56
1103	8/4/95	96 (109)	4.2	8	Philip	82
1106					Gertrude	28
1110	8/5/95	256 (76)	5.1	4	Philip	34
1112					Gertrude	19
1115	8/6/95	71 (20)	13.1	0	Philip	71
1123					Gertrude	20
1219	8/7/95	96 (29)	12.3	0	Philip	57
1242					Gertrude	19
1097	8/8/95	104 (45)	9.6	8	Philip	66
1099					Gertrude	42
1184	8/9/95	85 (46)	8.1	6	Philip	69
1207					Gertrude	34
1177	8/10/95	131 (69)	5.3	9	Philip	92
1179					Gertrude	58
1168	8/11/95	226 (26)	6.4	0	Philip	55
1167					Gertrude	23
1398	8/12/95	326 (45)	6.5	6	Philip	59
1399					Gertrude	20
none	8/13/95	46 (56)	7.0	3	Philip	n/a
1092					Gertrude	25
1086	8/14/95	59 (113)	4.5	6	Philip	65
1087					Gertrude	62
1007	8/15/95	296 (60)	5.1	5	Philip	141
1008					Gertrude	34
1129	8/16/95	51 (36)	4.3	9	Philip	72
1128					Gertrude	53
1388	8/17/95	58 (19)	5.1	3	Philip	73
1386					Gertrude	65
1018	8/18/95	76 (40)	5.9	3	Philip	72
1404					Gertrude	70
1011	8/19/95	45 (69)	6.8	6	Philip	49
1013					Gertrude	58
1419	8/20/95	26 (93)	6.1	4	Philip	54
1405					Gertrude	45
1498	4/10/96	255 (26)	8.7	4	Pier 25	87
1493	4/12/96	64 (20)	17.4	0	Pier 25	13
1491	4/14/96	93 (26)	12.1	1	Pier 25	8
1489	4/16/96	284 (6)	17.3	0	Pier 25	33

Appendix IV: Wind data and particulate (PM_{10}) concentrations for all air particulate filters collected for this study in Hamilton, 1995-1998

Filter #	Date	Average Wind Direction (std. dev.)	Average Wind Speed (km/hr)	# Hours Low Wind Speed - *1	Site - *2	Particulate Conc. (µg/m3)
1485	4/20/96	242 (12)	13.5	0	Pier 25	35
1380	4/23/96	273 (37)	11.3	0	Pier 25	21
1416	4/26/96	263 (17)	17.0	0	Pier 25	51
1411	5/1/96	231 (25)	9.2	3	Pier 25	33
1480	5/12/96	292 (18)	13.3	0	Pier 25	26
1479	5/13/96	246 (15)	9.7	3	Pier 25	50
1450	09/02/97	315 (36)	9.7	0	Dofasco	54
1449					Pool	23
1447	09/03/97	316 (18)	8.0	1	Dofasco	69
1448					Pool	24
1446	09/04/97	268 (31)	7.5	2	Dofasco	38
1445					Pool	50
1444	09/05/97	231 (18)	7.8	1	Dofasco	24
1443					Pool	29
1442	09/06/97	191 (108)	7.3	0	Dofasco	30
none					Pool	n/a
1441	09/07/97	61 (34)	9.9	0	Dofasco	25
none					Pool	n/a
1440	09/08/97	56 (44)	5.2	5	Dofasco	37
1439					Pool	19
1438	09/09/97	90 (30)	8.5	2	Dofasco	33
1437					Pool	24
1436	09/10/97	192 (50)	4.9	5	Dofasco	17
1435					Pool	30
1433	09/11/97	221 (14)	2.8	11	Dofasco	20
1432					Pool	25
1484	09/15/97	335 (63)	3.8	9	Dofasco	43
1431					Pool	20
1420	09/16/97	141 (64)	6.0	9	Dofasco	52
1430					Pool	34
1428	09/17/97	233 (29)	4.2	10	Dofasco	40
1427					Pool	23
1425	09/18/97	224 (19)	4.6	3	Dofasco	24
1426					Pool	31
1423	09/19/97	252 (54)	7.2	0	Dofasco	22
1422					Pool	20
1424	09/20/97	331 (15)	7.6	0	Dofasco	43
none					Pool	n/a
5001	09/21/97	230 (70)	5.2	11	Dofasco	17
none					Pool	n/a
5002	09/22/97	255 (17)	6.4	0	Dofasco	16
5000					Pool	45
5004	09/23/97	293 (52)	6.8	9	Dofasco	39
5003					Pool	22

Appendix IV: Wind data and particulate (PM_{10}) concentrations for all air particulate filters collected for this study in Hamilton, 1995-1998

Filter #	Date	Average Wind Direction (std. dev.)	Average Wind Speed (km/hr)	# Hours Low Wind Speed - *1	Site - *2	Particulate Conc. (µg/m3)
5006	09/24/97	224 (12)	6.0	0	Dofasco	16
5005					Pool	20
5007	09/25/97	334 (52)	9.2	0	Dofasco	34
5008					Pool	15
5009	09/29/97	254 (16)	11.9	0	Dofasco	33
5010					Pool	22
5011	10/01/97	302 (83)	3.4	9	Dofasco	26
5012					Pool	26
5013	10/02/97	221 (13)	4.4	2	Dofasco	21
5014					Pool	26
5015	10/06/97	140 (84)	1.6	21	Dofasco	60
5016					Pool	27
5017	10/07/97	35 (25)	3.1	15	Dofasco	48
5018					Pool	19
5019	10/08/97	69 (9)	3.8	16	Dofasco	63
5020					Pool	6
5030	05/08/98	70 (23)	4.5	9	Dofasco	54
5029					Pool	22
5032	05/09/98	58 (30)	7.1	2	Dofasco	16
5033					Pool	9
5034	05/10/98	56 (29)	6.5	1	Dofasco	5
5035					Pool	4
5036	05/11/98	75 (18)	7.8	6	Dofasco	8
5037					Pool	4
5039	05/12/98	43 (28)	4.5	9	Dofasco	46
5038					Pool	8
5041	05/13/98	31.1 (23)	2.8	16	Dofasco	107
5040					Pool	27
5043	05/14/98	156 (64)	3.2	16	Dofasco	165
none					Pool	n/a
5045	05/15/98	59 (38)	4.0	15	Dofasco	159
5042					Pool	77
5048	05/19/98	204 (93)	3.7	10	Dofasco	94
5047					Pool	73
5050	05/20/98	286 (17)	10.0	0	Dofasco	121
5049					Pool	94
5052	05/21/98	327 (19)	9.4	0	Dofasco	64
5051					Pool	28
5054	05/22/98	14 (88)	6.8	3	Dofasco	69
5053					Pool	25
5056	05/23/98	46 (98)	4.0	14	Dofasco	42
5055					Pool	28
5057	05/25/98	315 (96)	4.2	7	Dofasco	74
5058					Pool	37

Appendix IV: Wind data and particulate (PM_{10}) concentrations for all air particulate filters collected for this study in Hamilton, 1995-1998

Filter #	Date	Average Wind Direction (std. dev.)	Average Wind Speed (km/hr)	# Hours Low Wind Speed - *1	Site - *2	Particulate Conc. (µg/m3)
5059	05/26/98	55 (39)	3.9	14	Dofasco	73
5060					Pool	32
5061	05/27/98	153 (61)	4.0	12	Dofasco	88
6000					Pool	43
none	05/28/98	228 (12)	8.6	0	Dofasco	n/a
6002					Pool	67
6001	05/29/98	285 (44)	7.8	3	Dofasco	98
none					Pool	n/a
6004	05/30/98	104 (51)	6.7	8	Dofasco	31
6003					Pool	22
6006	06/1/98	237 (37)	5.6	2	Dofasco	49
6005					Pool	26
6008	06/2/98	257 (37)	12.3	0	Dofasco	89
6007					Pool	62
6010	06/3/98	280 (21)	9.3	0	Dofasco	50
6009					Pool	51
6012	06/4/98	291 (23)	9.7	1	Dofasco	93
6011					Pool	69
6014	06/5/98	340 (76)	7.8	0	Dofasco	57
6013					Pool	24
6015	06/6/98	291 (14)	10.0	0	Dofasco	46
6016					Pool	58
6018	06/8/98	290 (24)	5.0	11	Dofasco	51
6017					Pool	50
6019	06/9/98	79 (20)	5.2	9	Dofasco	34
6020					Pool	14
6021	06/11/98	46 (45)	4.1	8	Dofasco	38
6022					Pool	17
6024	06/12/98	229 (18)	8.4	0	Dofasco	42
6023					Pool	29
6026	06/13/98	279 (58)	4.0	6	Dofasco	27
6025					Pool	20
6028	06/15/98	148 (53)	2.7	16	Dofasco	66
6027					Pool	25
6030	06/16/98	162 (92)	4.1	5	Dofasco	52
6029					Pool	26
6032	06/17/98	292 (28)	8.0	0	Dofasco	49
6031					Pool	42
6033	06/18/98	349 (65)	3.3	14	Dofasco	45
6034					Pool	23
6036	06/19/98	58 (61)	3.5	13	Dofasco	55
none					Pool	n/a
6038	06/20/98	272 (40)	3.2	11	Dofasco	26
6037					Pool	42

Appendix IV: Wind data and particulate (PM_{10}) concentrations for all air particulate filters collected for this study in Hamilton, 1995-1998

Filter #	Date	Average Wind Direction (std. dev.)	Average Wind Speed (km/hr)	# Hours Low Wind Speed - *1	Site - *2	Particulate Conc. (µg/m3)
6040	06/22/98	209 (29)	3.9	10	Dofasco	72
6039					Pool	48
6042	06/23/98	60 (21)	2.6	16	Dofasco	53
6041					Pool	40
6043	06/24/98	177 (60)	5.4	7	Dofasco	83
6044					Pool	43
6045	06/25/98	205 (55)	5.3	3	Dofasco	59
6046					Pool	34
6048	06/26/98	275 (22)	10.9	2	Dofasco	47
6047					Pool	21
6050	06/29/98	250 (23)	8.5	4	Dofasco	65
6049					Pool	65
6052	06/30/98	323 (66)	8.2	1	Dofasco	25
6051					Pool	16
6053	07/1/98	313 (27)	7.3	5	Dofasco	66
6054					Pool	48
6056	07/2/98	189 (61)	2.8	13	Dofasco	73
6055					Pool	51
6058	07/6/98	60 (30)	5.9	5	Dofasco	26
6057					Pool	10
6060	07/7/98	30 (21)	5.6	0	Dofasco	15
6059					Pool	13
6063	07/9/98	362 (71)	5.7	5	Dofasco	10
none					Pool	n/a

*1 - low wind speed defined as < 3 km/hr

*2 - for site location, refer to Map 2.2

Note: wind data obtained from the MOE stn 29026 (see Map 2.2)

Appendix V: Concentrations of PAC in source samples (ng/g)

Appendix V: PAC concentrations in source samples (ng/g). Sample descriptions correspond to sample names in Appendix II.

GC-MS Data File	AN220T7B	AN234T7B	AN299T7B	AN326T7B	N3308	AN550T7D	AN650T7B
Sample Description	N220	N234	N299	N326	N330	N550	N650
Extracting Solvent	TOL	TOL	TOL	TOL	TOL	TOL	TOL
Mass Particulate in vial (g)	0.02	0.02	0.02	0.02	0.02	0.02	0.02
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	<0.3	192.5	<0.3	<0.3	<0.3	<0.3	<0.3
Phenanthrene	<0.5	1510.8	404.5	99.6	<0.5	<0.5	298.6
Anthracene	<0.3	145.8	<0.3	<0.3	<0.3	<0.3	<0.3
o-Terphenyl	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7
1-Methylphenanthrene	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Anthraquinone	<2	<2	<2	<2	<2	<2	<2
Fluoranthene	3913.2	52513.7	24907.5	3430.1	14800.0	958.6	7937.2
Pyrene	55840.9	280029.8	219639.5	61779.4	150000.0	30828.0	166198.8
m-Terphenyl	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7
p-Terphenyl	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Benzo[a]fluorene	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Benzo[b]fluorene	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
B21T	22.3	454.4	58.0	<0.5	<0.5	56.3	25.5
Benzo[ghi]fluoranthene	12236.5	63176.2	45977.8	8924.9	21100.0	1892.8	8273.7
Benzo[c]phenanthrene	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7
B23T	<0.5	167.4	<0.5	<0.5	<0.5	<0.5	<0.5
Benz[a]anthracene	<0.5	295.2	<0.5	61.2	<0.5	<0.5	50.0
Cyclopenta[cd]pyrene	2354.4	53090.3	56422.1	97.0	7660.0	<0.7	15271.2
Chrysene	<0.5	430.5	<0.5	124.9	<0.5	158.5	138.1
Benzanthrone	<1	277.6	<1	78.9	<1	<1	64.7
2-Nitrofluoranthene	<4	<4	<4	<4	<4	<4	<4
B[a]A-7,12-dione	<2	<2	<2	<2	<2	<2	<2
Benzo[b]fluoranthene	63.1	1516.7	387.3	129.0	110.0	55.3	185.8
Benzo[k]fluoranthene	<0.5	483.1	150.7	48.7	<0.5	<0.5	63.5
Benzo[j]fluoranthene	<0.5	449.9	124.9	52.0	<0.5	<0.5	48.1
Benzo[e]pyrene	634.4	5525.7	3298.8	775.8	1730.0	248.9	1810.4
Benzo[a]pyrene	325.1	4704.5	2490.4	205.3	930.0	<0.7	1523.6
Perylene	<0.7	620.9	287.8	<0.7	80.0	<0.7	200.4
Indeno[1,2,3-cd]pyrene	314.0	5915.1	2775.7	232.4	2050.0	102.4	1685.0
Dibenz[ac]anthracene	258.9	112.8	<1	65.1	<1	<1	<1
Picene	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7
Benzo[ghi]perylene	13467.6	74173.6	50334.0	6715.4	<0.8	4273.8	26856.5
Coronene	20141.2	83221.3	45129.0	3540.4	64200.0	9828.7	28570.0
Dibenzo[a,e]pyrene	605.4	2599.9	1267.6	110.8	<0.9	282.1	871.9
Dibenzo[a,i]pyrene	<1	<1	<1	<1	<1	<1	<1
Dibenzo[a,h]pyrene	<1	<1	<1	<1	<1	<1	<1
Thiacoronene	10764.9	40142.2	17500.6	2188.8	17800.0	4422.8	9218.5
Total PAC (µg/g)	120.94	671.75	471.16	88.66	280.46	53.11	269.29

GC-MS Data File	AN660T7B	AR820T7B	AC115T7A	C1489T7A	C7011T7A	DSLSTEDA	DSLSTETA
Sample Description	N660	R820	C1150	C1489	C7011	DSLSTE	DSLSTE
Extracting Solvent	TOL	TOL	TOL	TOL	TOL	DCM	TOL
Mass Particulate in vial (g)	0.02	0.02	0.25	0.20	0.20	0.01	0.01
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	<0.3	<0.3	<0.3	0.5	<0.3	<0.3	138.1
Phenanthrene	1874.5	1982.0	<0.5	337.6	6.2	4340.7	4220.6
Anthracene	<0.3	<0.3	<0.3	20.4	<0.3	<0.3	5021.4
o-Terphenyl	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	38.8
1-Methylphenanthrene	<0.8	<0.8	<0.8	<0.8	<0.8	11875.5	700.3
Anthraquinone	<2	<2	<2	<2	<2	6360.8	1234.9
Fluoranthene	59767.9	57052.6	9.4	40.8	52.8	78386.1	4610.9
Pyrene	574111.5	417153.6	68.2	706.5	932.6	142467.3	3241.4
m-Terphenyl	<0.7	<0.7	<0.7	<0.7	<0.7	998.5	63.5
p-Terphenyl	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	45.6
Benzo[a]fluorene	<0.8	<0.8	<0.8	<0.8	<0.8	7232.4	236.4
Benzo[b]fluorene	<0.9	<0.9	<0.9	<0.9	<0.9	2374.7	95.4
B21T	<0.5	<0.5	<0.5	<0.5	<0.5	6065.5	426.7
Benzo[ghi]fluoranthene	37665.3	80801.4	<0.6	16.3	45.2	48519.7	924.8
Benzo[c]phenanthrene	<0.7	<0.7	<0.7	<0.7	<0.7	6849.6	219.2
B23T	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Benz[a]anthracene	192.9	<0.5	<0.5	1.5	1.0	27802.8	957.6
Cyclopenta[cd]pyrene	84123.4	117077.2	<0.7	<0.7	<0.7	<0.7	<0.7
Chrysene	619.4	246.1	<0.5	<0.5	<0.5	36935.6	3146.6
Benzanthrone	<1	282.7	<1	<1	<1	9728.3	534.4
2-Nitrofluoranthene	<4	<4	<4	<4	<4	<4	<4
B[a]A-7,12-dione	<2	<2	<2	<2	<2	1013.8	216.0
Benzo[b]fluoranthene	1308.8	881.1	<0.7	2.1	3.5	10410.6	1853.0
Benzo[k]fluoranthene	557.9	268.6	<0.5	0.8	1.2	4543.9	976.9
Benzo[j]fluoranthene	371.2	422.9	<0.5	0.8	0.8	6839.3	1020.6
Benzo[e]pyrene	10504.7	7719.7	<0.6	4.0	7.4	10054.3	1241.8
Benzo[a]pyrene	8709.9	9366.2	<0.7	2.6	1.7	5880.9	80.4
Perylene	1269.7	769.5	<0.7	1.9	2.0	1119.3	<0.7
Indeno[1,2,3-cd]pyrene	11372.6	13410.9	<0.7	1.7	2.6	4086.4	3041.0
Dibenz[ac]anthracene	714.6	309.1	<1	<1	<1	3134.2	201.1
Picene	<0.7	<0.7	<0.7	<0.7	<0.7	302.1	456.0
Benzo[ghi]perylene	114004.0	128484.8	<0.8	19.3	22.6	10793.2	1892.3
Coronene	48822.7	117396.3	<0.8	8.0	8.3	3782.2	2002.7
Dibenzo[a,e]pyrene	1375.1	3487.3	<0.9	<0.9	<0.9	455.7	157.6
Dibenzo[a,i]pyrene	<1	<1	<1	<1	<1	469.5	243.6
Dibenzo[a,h]pyrene	<1	<1	<1	<1	<1	59.6	<1
Thiacoronene	14931.8	43493.1	<0.3	5.2	4.3	<0.3	<0.3
Total PAC (µg/g)	972.30	1000.60	0.08	1.17	1.09	452.88	39.24

GC-MS Data File	DSLSHEDA	DSLSHETA	DSLWVUDA	DSLWVUTB	DSLCBDDA	DSLCBDTB	1650M97A
Sample Description	DSLSHE	DSLSHE	DSLWVU	DSLWVU	DSLCBD	DSLCBD	SRM1650
Extracting Solvent	DCM	TOL	DCM	TOL	DCM	TOL	DCM
Mass Particulate in vial (g)	0.01	0.01	0.01	0.01	0.01	0.01	
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	7726.4
Phenanthrene	9561.7	2410.7	15554.0	199.5	4905.4	169.5	50230.2
Anthracene	1342.6	339.4	1397.0	73.5	275.0	431.1	1193.0
o-Terphenyl	<0.7	27.0	<0.7	<0.7	<0.7	<0.7	13.3
1-Methylphenanthrene	29742.3	570.9	37785.8	195.6	20510.2	186.3	20674.9
Anthraquinone	11281.5	657.8	11393.6	533.9	<2	477.4	11600.7
Fluoranthene	62552.2	1446.0	77484.8	994.4	54662.5	830.2	51218.3
Pyrene	107884.7	109.6	130021.9	1378.9	99979.3	772.6	49601.0
m-Terphenyl	3003.3	38.7	2382.4	33.9	2747.7	33.8	609.1
p-Terphenyl	1145.5	39.6	898.1	37.0	<0.8	38.8	417.5
Benzo[a]fluorene	10775.6	114.9	7725.5	254.8	<0.8	196.2	1826.1
Benzo[b]fluorene	4975.4	<0.9	3387.0	108.8	<0.9	97.0	384.0
B21T	6306.4	110.0	4555.3	73.9	<0.5	117.5	4768.7
Benzo[ghi]fluoranthene	28832.3	600.3	28086.2	718.7	27864.5	642.3	12620.1
Benzo[c]phenanthrene	4858.8	98.2	4567.2	132.5	4849.5	115.3	1990.3
B23T	28057.9	<0.5	16564.5	<0.5	<0.5	<0.5	418.7
Benz[a]anthracene	21744.8	<0.5	17884.9	1144.0	21379.3	595.3	5668.0
Cyclopenta[cd]pyrene	13119.1	<0.7	4128.5	331.3	5019.8	23.2	<0.7
Chrysene	30944.7	1723.2	24385.0	1660.3	30317.8	1882.0	<0.5
Benzanthrone	5864.8	416.6	6118.0	279.3	6628.3	372.3	<1
2-Nitrofluoranthene	<4	<4	<4	<4	<4	<4	<4
B[a]A-7,12-dione	447.9	231.8	514.2	92.5	389.4	138.2	3475.9
Benzo[b]fluoranthene	6483.9	1095.5	6142.7	823.7	7212.8	1073.8	13869.5
Benzo[k]fluoranthene	3073.6	300.6	2723.4	279.7	3213.5	590.2	5208.5
Benzo[j]fluoranthene	4441.7	244.9	3946.6	537.2	4868.3	637.2	6217.0
Benzo[e]pyrene	6200.5	298.2	5999.0	515.4	6789.4	581.8	12635.4
Benzo[a]pyrene	5682.0	296.6	5041.7	25.5	6258.7	<0.7	1345.3
Perylene	995.7	30.5	976.3	<0.7	1059.7	<0.7	<0.7
Indeno[1,2,3-cd]pyrene	3962.2	439.6	4129.5	2065.4	5137.4	2207.8	6259.1
Dibenz[ac]anthracene	<1	<1	<1	490.1	1647.9	<1	557.4
Picene	172.6	210.0	167.9	208.3	242.8	239.0	<0.7
Benzo[ghi]perylene	6540.4	35.6	6961.9	1061.7	7818.3	1468.4	7793.4
Coronene	1706.7	1264.7	1693.0	2412.7	1943.5	1749.3	2480.6
Dibenzo[a,e]pyrene	248.5	84.2	260.1	154.9	271.7	92.0	208.3
Dibenzo[a,i]pyrene	256.2	34.1	220.1	126.3	301.9	110.1	137.6
Dibenzo[a,h]pyrene	120.3	60.6	113.7	<1	165.3	<1	<1
Thiacoronene	19.6	<0.3	22.7	<0.3	40.6	<0.3	60.9
Total PAC (µg/g)	422.33	13.33	433.21	16.94	326.46	15.87	281.15

GC-MS Data File	1650TSMA	404GBDSA	404GBTSA	STCQDA1	STCQTA1	STCADA1	STCATA1
Sample Description	SRM1650	404GB	404GB	STCQ	STCQ	STCA	STCA
Extracting Solvent	TOL	DCM	TOL	DCM	TOL	DCM	TOL
Mass Particulate in vial (g)	0.01	0.17	0.17	0.40	0.40	0.10	0.10
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	<0.3	679.9	72.3	108.7	12.1	524.8	25.9
Phenanthrene	461.4	1808.5	118.0	2551.9	1138.8	5965.2	10960.9
Anthracene	<0.3	199.1	8.3	537.9	23.7	164.3	146.0
o-Terphenyl	<0.7	75.4	<0.7	1.8	<0.7	1.6	<0.7
1-Methylphenanthrene	1284.6	267.1	41.7	673.7	179.1	1517.8	2301.8
Anthraquinone	1931.9	481.0	182.7	147.0	177.0	31.4	17.4
Fluoranthene	3599.2	3002.9	491.8	2285.7	641.2	551.9	328.7
Pyrene	5205.7	2787.1	492.3	5981.0	400.5	665.2	605.8
m-Terphenyl	209.7	100.7	14.2	23.3	6.2	51.6	128.1
p-Terphenyl	179.9	143.2	12.6	15.1	4.5	43.8	118.9
Benzo[a]fluorene	551.1	151.5	29.9	260.6	50.1	1035.7	1831.7
Benzo[b]fluorene	381.6	89.8	17.1	97.1	14.9	284.4	540.5
B21T	770.8	466.5	81.5	233.0	24.9	502.9	215.1
Benzo[ghi]fluoranthene	1159.1	1393.5	255.1	222.5	41.5	16.7	<0.6
Benzo[c]phenanthrene	170.8	164.9	32.5	109.5	23.6	22.3	<0.7
B23T	115.2	136.9	<0.5	65.8	4.5	51.4	<0.5
Benz[a]anthracene	1182.2	2111.9	446.0	1015.7	165.3	254.5	250.0
Cyclopenta[cd]pyrene	34.7	330.4	80.4	98.2	<0.7	10.2	<0.7
Chrysene	3480.3	4294.0	796.0	1375.0	297.8	1253.3	1799.5
Benzanthrone	751.6	803.2	191.8	114.9	37.8	<1	<1
2-Nitrofluoranthene	<4	<4	<4	<4	<4	<4	<4
B[a]A-7,12-dione	146.6	307.3	71.9	<2	<2	<2	<2
Benzo[b]fluoranthene	625.1	2191.3	327.8	596.0	129.1	292.6	219.8
Benzo[k]fluoranthene	242.8	801.4	147.0	305.7	64.6	48.4	65.5
Benzo[j]fluoranthene	223.6	990.3	142.6	301.2	57.8	44.6	45.3
Benzo[e]pyrene	614.8	1759.3	234.9	525.8	80.9	419.0	206.6
Benzo[a]pyrene	207.8	800.9	114.8	500.6	3.5	143.1	51.0
Perylene	34.9	166.4	15.7	105.5	<0.7	20.2	<0.7
Indeno[1,2,3-cd]pyrene	1212.2	2271.5	394.6	329.2	91.1	67.7	26.3
Dibenz[ac]anthracene	153.8	466.2	74.3	46.1	<1	35.4	<1
Picene	<0.7	179.6	36.4	59.4	27.1	54.5	53.8
Benzo[ghi]perylene	1914.7	4536.8	637.2	416.5	74.6	266.7	96.8
Coronene	2145.9	3343.6	528.3	97.0	33.2	87.2	22.4
Dibenzo[a,e]pyrene	160.5	261.8	37.9	65.6	12.8	85.8	27.1
Dibenzo[a,i]pyrene	<1	173.5	36.9	59.2	18.9	84.0	36.1
Dibenzo[a,h]pyrene	<1	<1	<1	37.6	<1	8.9	<1
Thiacoronene	30.5	108.9	11.8	4.5	1.2	<0.3	<0.3
Total PAC (μg/g)	29.15	37.74	6.16	19.36	3.84	14.61	20.12

GC-MS Data File	STDADB	STDATB	ABSTDBDA	STSBDSMA	STSBTSMA	STSPDSMA	STSPTSMA
Sample Description	STDA	STDA	STDB	STSB	STSB	STSP	STSP
Extracting Solvent	DCM	TOL	DCM	DCM	TOL	DCM	TOL
Mass Particulate in vial (g)	1.87	1.87	0.03	1.94	1.94	2.52	2.52
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	251.7	75.8	<0.3	5.2	<0.3	<0.3	<0.3
Phenanthrene	3693.2	900.2	136.6	54.9	28.0	<0.5	<0.5
Anthracene	758.3	298.7	77.3	<0.3	2.1	<0.3	<0.3
o-Terphenyl	<0.7	<0.7	<0.7	0.7	0.7	<0.7	<0.7
1-Methylphenanthrene	1828.3	264.8	219.6	13.4	1.4	<0.8	<0.8
Anthraquinone	229.2	62.9	<2	45.2	10.0	0.7	<2
Fluoranthene	6683.6	796.2	181.8	161.9	9.2	1.2	<0.4
Pyrene	7285.7	623.3	224.9	51.6	0.0	0.6	<0.4
m-Terphenyl	131.1	33.5	<0.7	7.9	1.2	0.8	<0.7
p-Terphenyl	69.6	31.7	<0.8	3.5	0.5	<0.8	<0.8
Benzo[a]fluorene	231.6	75.8	96.5	1.2	<0.8	<0.8	<0.8
Benzo[b]fluorene	68.0	32.6	<0.9	<0.9	<0.9	<0.9	<0.9
B21T	1926.2	254.0	91.8	255.5	<0.5	0.7	<0.5
Benzo[ghi]fluoranthene	851.9	68.4	18.6	13.1	<0.6	0.7	<0.6
Benzo[c]phenanthrene	410.8	43.3	<0.7	6.9	<0.7	<0.7	<0.7
B23T	539.6	55.0	<0.5	25.0	<0.5	<0.5	<0.5
Benz[a]anthracene	4413.6	690.9	111.5	27.8	<0.5	0.8	<0.5
Cyclopenta[cd]pyrene		39.0	<0.7	<0.7	3.6	<0.7	<0.7
Chrysene	6832.0	813.4	101.3	424.0	14.0	3.0	<0.5
Benzanthrone	484.3	38.6	<1	30.5	1.0	21.2	<1
2-Nitrofluoranthene	<4	<4	<4	<4	<4	<4	<4
B[a]A-7,12-dione	197.9	20.7	<2	17.2	2.0	<2	<2
Benzo[b]fluoranthene	1585.5	163.6	109.3	51.4	4.4	0.4	0.3
Benzo[k]fluoranthene	538.9	65.8	87.9	6.4	<0.5	<0.5	<0.5
Benzo[j]fluoranthene	663.3	73.1	50.9	5.3	<0.5	<0.5	<0.5
Benzo[e]pyrene	1970.9	152.4	241.0	29.0	0.4	0.4	<0.6
Benzo[a]pyrene	1031.1	123.2	103.9	3.1	<0.7	<0.7	<0.7
Perylene	201.5	22.3	<0.7	1.0	<0.7	<0.7	<0.7
Indeno[1,2,3-cd]pyrene	912.1	105.6	53.0	4.5	<0.7	<0.7	<0.7
Dibenz[ac]anthracene	326.6	20.4	<1	2.5	<1	<1	<1
Picene	187.9	32.4	<0.7	3.5	1.4	0.0	<0.7
Benzo[ghi]perylene	1617.2	137.9	165.8	7.3	<0.8	0.4	<0.8
Coronene	557.2	64.5	37.7	1.9	<0.8	<0.8	<0.8
Dibenzo[a,e]pyrene	441.6	48.6	<0.9	<0.9	<0.9	<0.9	<0.9
Dibenzo[a,i]pyrene	286.3	51.5	<1	<1	<1	<1	<1
Dibenzo[a,h]pyrene	127.8	23.1	<1	<1	<1	<1	<1
Thiacoronene	30.6	2.8	<0.3	0.3	<0.3	<0.3	<0.3
Total PAC (µg/g)	47.33	6.30	2.11	1.26	0.08	0.03	0.00

GC-MS Data File	STSSDSMA	STSSTSMA	ABDOD1DA	ABDOD2DA	ADOD2TA1	ADOCBADA	DOCBATA1
Sample Description	STSS	STSS	ABDOD1	ABDOD2	ADOD2	ADOCBA	DOCBA
Extracting Solvent	DCM	TOL	DCM	DCM	TOL	DCM	TOL
Mass Particulate in vial (g)	5.60	5.60	0.03	0.03	0.40	0.03	0.40
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	306.9	2.4	2233.0	748.2	2.4	1125.3	60.5
Phenanthrene	2674.8	147.4	11294.1	7149.8	48.7	20298.6	1182.7
Anthracene	167.9	114.4	747.9	1322.3	7.3	5285.7	320.3
o-Terphenyl	<0.7	<0.7	5.0	3.6	<0.7	4.2	<0.7
1-Methylphenanthrene	359.9	41.2	5912.5	2403.1	63.5	3931.3	152.7
Anthraquinone	193.5	39.6	588.9	<2	22.2	336.7	46.9
Fluoranthene	2927.5	313.0	5378.2	10894.8	273.8	27407.5	1738.7
Pyrene	2107.3	112.3	11394.2	13101.4	271.2	23448.7	1265.6
m-Terphenyl	<0.7	8.5	149.1	108.0	4.5	140.2	7.8
p-Terphenyl	<0.8	5.8	84.2	62.3	4.1	76.9	5.4
Benzo[a]fluorene	171.7	7.4	152.6	698.7	9.1	2406.7	51.2
Benzo[b]fluorene	20.0	1.5	110.4	311.9	2.9	1190.5	19.2
B21T	566.7	2.4	3274.8	2780.2	102.2	2744.1	187.5
Benzo[ghi]fluoranthene	211.0	17.6	659.3	1218.2	19.7	2090.5	101.6
Benzo[c]phenanthrene	<0.7	10.6	<0.7	427.2	12.6	1179.3	77.8
B23T	134.5	<0.5	624.9	673.9	21.9	859.4	61.5
Benz[a]anthracene	938.3	11.6	3696.9	6795.2	188.8	14797.6	1145.9
Cyclopenta[cd]pyrene	<0.7	<0.7	<0.7	<0.7	<0.7	382.6	8.3
Chrysene	1704.1	203.6	3635.2	6801.1	349.9	14803.5	1026.2
Benzanthrone	46.5	39.8	2223.7	1746.1	48.8	855.0	46.3
2-Nitrofluoranthene	<4	<4	<4	<4	<4	<4	<4
B[a]A-7,12-dione	32.4	124.3	1774.1	1148.8	<2	219.7	<2
Benzo[b]fluoranthene	426.2	404.7	2634.1	6130.4	90.1	15357.6	528.0
Benzo[k]fluoranthene	184.3	156.8	959.8	3163.9	51.4	8762.3	361.4
Benzo[j]fluoranthene	169.3	129.3	582.2	2413.5	37.1	8055.2	269.9
Benzo[e]pyrene	393.8	281.0	4563.0	6844.7	72.5	13871.8	339.8
Benzo[a]pyrene	205.6	<0.7	2288.1	6495.9	86.3	17538.1	677.2
Perylene	55.5	<0.7	788.7	1852.6	16.4	4657.3	135.8
Indeno[1,2,3-cd]pyrene	274.4	111.0	1065.9	4068.2	57.7	12592.4	438.4
Dibenz[ac]anthracene	90.8	20.2	570.9	1248.9	11.0	2335.6	84.7
Picene	49.5	56.5	450.4	827.4	19.2	2115.6	122.0
Benzo[ghi]perylene	360.7	73.8	2589.0	5618.6	59.5	15146.8	407.2
Coronene	106.8	63.9	314.1	1042.4	12.2	3662.1	101.4
Dibenzo[a,e]pyrene	78.3	2.3	228.8	822.1	8.7	3221.7	98.5
Dibenzo[a,i]pyrene	80.3	29.7	367.8	966.9	15.0	3266.2	139.1
Dibenzo[a,h]pyrene	40.3	<1	75.7	445.2	4.1	237.4	110.8
Thiacoronene	6.7	1.3	8.1	46.6	0.7	168.9	4.8
Total PAC (μg/g)	15.08	2.53	71.42	100.34	1.99	234.40	11.32

GC-MS Data File	ADOPEMDA	DOPEMTA1	ADOPINDA	DOPINTA1	DOEGUDB	DOEGUTA	DOMASDSA
Sample Description	ADOPEM	DOPEM	ADOPIN	DOPIN	DOEGU	DOEGU	DOMAS
Extracting Solvent	DCM	TOL	DCM	TOL	DCM	TOL	DCM
Mass Particulate in vial (g)	0.03	0.40	0.03	0.40	1.79	1.79	1.84
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	630.3	146.6	180.1	88.3	292.6	<0.3	273.6
Phenanthrene	15888.3	3465.0	1247.9	741.7	1409.8	34.1	4256.4
Anthracene	1675.7	<0.3	274.0	68.2	127.7	<0.3	40.1
o-Terphenyl	<0.7	<0.7	<0.7	<0.7	33.7	<0.7	<0.7
1-Methylphenanthrene	1028.0	99.6	471.2	196.6	315.6	128.0	1522.0
Anthraquinone	1815.2	291.4	<2	<2	67.0	<2	<2
Fluoranthene	24617.8	2092.4	411.5	73.7	524.5	161.1	615.6
Pyrene	16898.7	764.0	527.3	75.8	531.4	214.7	911.4
m-Terphenyl	28.4	3.2	66.5	33.5	97.6	115.0	<0.7
p-Terphenyl	16.5	2.1	63.6	34.8	107.8	136.0	<0.8
Benzo[a]fluorene	86.1	10.5	710.5	263.7	459.0	656.3	964.0
Benzo[b]fluorene	11.7	2.5	198.0	80.2	210.9	235.1	208.0
B21T	1025.5	118.7	509.6	201.1	647.4	736.4	670.8
Benzo[ghi]fluoranthene	1483.5	114.9	<0.6	<0.6	112.3	20.3	<0.6
Benzo[c]phenanthrene	461.2	56.7	<0.7	<0.7	57.2	26.5	<0.7
B23T	232.0	15.8	27.1	9.9	124.4	4.5	96.7
Benz[a]anthracene	3775.1	142.5	158.2	23.7	220.4	46.5	457.7
Cyclopenta[cd]pyrene	<0.7	<0.7	<0.7	<0.7	47.3	<0.7	<0.7
Chrysene	3775.3	831.5	140.2	358.0	1457.7	1574.0	2052.2
Benzanthrone	406.6	32.4	<1	<1	119.0	<1	44.9
2-Nitrofluoranthene	<4	<4	<4	<4	<4	<4	<4
B[a]A-7,12-dione	732.7	<2	<2	<2	32.0	<2	<2
Benzo[b]fluoranthene	5149.4	869.9	378.2	36.9	260.5	131.0	267.2
Benzo[k]fluoranthene	2980.5	391.8	148.8	10.5	58.5	10.3	45.1
Benzo[j]fluoranthene	2510.4	319.0	83.5	5.1	49.7	3.3	45.9
Benzo[e]pyrene	4450.2	526.0	451.8	27.7	287.8	77.6	557.3
Benzo[a]pyrene	1258.1	<0.7	245.3	15.5	63.3	12.2	148.1
Perylene	222.2	<0.7	36.1	1.2	38.9	<0.7	<0.7
Indeno[1,2,3-cd]pyrene	1844.2	906.4	146.8	4.8	102.8	10.9	68.0
Dibenz[ac]anthracene	183.5	55.7	<1	<1	72.6		48.2
Picene	99.4	134.9	62.4	11.6	76.9	40.1	43.8
Benzo[ghi]perylene	1869.5	855.3	293.6	11.8	205.4	27.7	364.6
Coronene	161.6	232.9	84.0	2.8	105.3	7.8	141.1
Dibenzo[a,e]pyrene	<0.9	16.8	95.3	4.2	103.1	10.4	117.1
Dibenzo[a,i]pyrene	<1	57.6	73.0	6.0	118.7	22.6	137.6
Dibenzo[a,h]pyrene	<1	<1	<1	<1	32.3	<1	<1
Thiacoronene	15.0	20.6	<0.3	<0.3	<0.3	<0.3	<0.3
Total PAC (µg/g)	95.32	12.56	7.08	2.39	8.57	4.44	14.10

GC-MS Data File	DOMASTSA	MONDSDSA	MONDSTSA	MOPHLDSA	MOPHLTSA	MOWSTDSA	MOWSTTSA
Sample Description	DOMAS	MONDS	MONDS	MOPHL	MOPHL	MOWST	MOWST
Extracting Solvent	TOL	DCM	TOL	DCM	TOL	DCM	TOL
Mass Particulate in vial (g)	1.84	2.85	2.85	5.58	5.57	4.26	4.26
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	45.7	40.3	2.1	57.2	<0.3	89.0	<0.3
Phenanthrene	3800.3	1004.5	94.6	699.2	163.7	2486.1	128.2
Anthracene	<0.3	144.3	<0.3	53.6	<0.3	147.5	<0.3
o-Terphenyl	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7
1-Methylphenanthrene	1819.7	64.6	8.9	116.7	31.1	274.4	20.5
Anthraquinone	<2	101.3	16.0	69.0	39.9	323.0	19.2
Fluoranthene	345.9	3012.0	135.5	1787.9	352.2	6667.9	262.8
Pyrene	632.0	2228.2	47.8	1786.8	248.4	4938.4	74.4
m-Terphenyl	35.1	4.2	2.0	12.6	10.5	<0.7	3.7
p-Terphenyl	22.9	<0.8	1.3	7.7	7.0	<0.8	1.5
Benzo[a]fluorene	1183.1	128.8	3.5	19.5	3.4	296.1	4.8
Benzo[b]fluorene	203.8	69.8	1.2	9.9	1.1	126.4	<0.9
B21T	274.6	279.5	3.6	219.2	4.6	574.6	3.0
Benzo[ghi]fluoranthene	<0.6	201.0	9.9	203.8	38.9	427.6	15.6
Benzo[c]phenanthrene	61.6	109.6	4.3	69.9	12.2	285.0	9.3
B23T	0.0	56.3	1.1	48.2	<0.5	153.5	<0.5
Benz[a]anthracene	312.4	1088.3	9.1	539.2	53.4	2391.4	15.4
Cyclopenta[cd]pyrene	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7
Chrysene	1521.7	1623.1	77.0	1123.6	212.0	3583.1	139.3
Benzanthrone	<1	24.6	4.8	20.1	4.9	40.1	1.5
2-Nitrofluoranthene	<4	<4	<4	<4	<4	<4	<4
B[a]A-7,12-dione	22.3	20.0	13.9	20.9	14.7	60.6	8.0
Benzo[b]fluoranthene	165.5	508.7	63.6	335.4	50.4	1096.3	23.8
Benzo[k]fluoranthene	33.1	293.3	21.4	156.9	28.3	588.1	10.7
Benzo[j]fluoranthene	19.4	252.7	19.5	136.7	21.6	509.5	7.3
Benzo[e]pyrene	269.2	425.4	37.6	297.9	25.1	812.7	11.3
Benzo[a]pyrene	57.5	459.7	3.3	165.9	<0.7	739.0	<0.7
Perylene	<0.7	128.9	0.7	53.6	<0.7	209.9	<0.7
Indeno[1,2,3-cd]pyrene	33.3	484.7	25.8	264.7	34.3	832.4	7.3
Dibenz[ac]anthracene	23.9	99.6	3.6	73.3	6.2	<1	<1
Picene	23.1	69.0	8.6	39.5	11.1	149.3	3.3
Benzo[ghi]perylene	189.4	512.2	27.7	374.3	21.9	862.9	3.1
Coronene	69.2	160.6	22.2	193.2	26.6	230.5	3.5
Dibenzo[a,e]pyrene	47.8	88.6	2.0	52.2	2.7	164.8	<0.9
Dibenzo[a,i]pyrene	54.4	104.4	<1	56.0	3.9	185.1	<1
Dibenzo[a,h]pyrene	<1	<1	<1	25.2	<1	91.7	<1
Thiacoronene	<0.3	20.5	2.7	49.5	1.4	23.4	<0.3
Total PAC (μg/g)	11.27	13.79	0.67	9.09	1.43	29.34	0.78

GC-MS Data File	MOWCCDA	MOWCCTA	DETECTION
Sample Description	MOWCC	MOWCC	LIMITS
Extracting Solvent	DCM	TOL	
Mass Particulate in vial (g)	5.86	5.86	
	(ng/g)	(ng/g)	(ng/g)
Dibenzothiophene	380.6	12.9	<0.3
Phenanthrene	10108.9	540.9	<0.5
Anthracene	4151.6	<0.3	<0.3
o-Terphenyl	<0.7	<0.7	<0.7
1-Methylphenanthrene	590.2	57.4	<0.8
Anthraquinone	3105.1	465.2	<2
Fluoranthene	31241.6	2003.6	<0.4
Pyrene	23181.2	964.2	<0.4
m-Terphenyl	48.5	10.5	<0.7
p-Terphenyl	27.2	6.2	<0.8
Benzo[a]fluorene	871.1	6.9	<0.8
Benzo[b]fluorene	653.7	5.2	<0.9
B21T	3238.7	186.6	<0.5
Benzo[ghi]fluoranthene	2327.9	91.8	<0.6
Benzo[c]phenanthrene	1405.9	68.6	<0.7
B23T	774.1	6.6	<0.5
Benz[a]anthracene	10980.1	283.7	<0.5
Cyclopenta[cd]pyrene	94.0	<0.7	<0.7
Chrysene	18780.2	1167.9	<0.5
Benzanthrone	305.6	19.7	<1
2-Nitrofluoranthene	<4	<4	<4
B[a]A-7,12-dione	328.6	51.1	<2
Benzo[b]fluoranthene	6377.0	208.5	<0.7
Benzo[k]fluoranthene	3194.6	102.3	<0.5
Benzo[j]fluoranthene	2808.0	84.5	<0.5
Benzo[e]pyrene	4637.9	102.2	<0.6
Benzo[a]pyrene	4009.4	3.3	<0.7
Perylene	1259.7	2.7	<0.7
Indeno[1,2,3-cd]pyrene	5161.6	94.9	<0.7
Dibenz[ac]anthracene	665.6	15.5	<1
Picene	781.0	24.3	<0.7
Benzo[ghi]perylene	5136.1	68.2	<0.8
Coronene	1319.1	15.5	<0.8
Dibenzo[a,e]pyrene	990.3	5.1	<0.9
Dibenzo[a,i]pyrene	1279.8	10.8	<1
Dibenzo[a,h]pyrene	791.4	<1	<1
Thiacoronene	84.8	1.7	<0.3
Total PAC (µg/g)	151.01	6.69	

Appendix VI: Concentrations of PAC in ambient air samples (ng/m^3)

Appendix VI: PAC concentrations in dichloromethane extracts of ambient air samples (pg/m3)

Date Collected	July 14/95	July 17/95	July 18/95	July 19/95	July 20/95	July 23/95	July 29/95
Sampling Site	Philip	Philip	Philip	Philip	Philip	Philip	Philip
GC-MS Data File	PHLJL14D	PHLJL17D	PHLJL18D	PHLJL19D	PHLJL20D	PHLJL23D	PHLJL29D
Volume of Air (m3)	1637	1434	1433	1434	1434	1434	1434
Mass Particulate (g)	0.119	0.122	0.225	0.138	0.180	0.055	0.073
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	DCM	DCM
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	21.1	28.1	42.5	18.3	46.9	18.4	11.6
Phenanthrene	414.6	501.5	784.0	377.1	781.7	282.3	236.0
Anthracene	39.1	94.5	100.5	64.4	78.1	45.1	50.5
o-Terphenyl	0.7	0.9	2.4	1.0	4.8	3.9	1.5
1-Methylphenanthrene	51.4	82.3	127.5	96.8	75.5	37.3	46.7
Anthraquinone	183.7	211.7	260.1	309.6	156.6	75.4	128.8
Fluoranthene	1419.2	2670.5	4087.7	3891.2	2524.9	756.3	1858.6
Pyrene	1207.5	2476.5	4157.8	4108.3	3117.9	759.1	1915.0
m-Terphenyl	6.5	8.6	15.0	12.3	11.9	7.3	8.0
p-Terphenyl	4.3	6.0	11.2	8.0	8.4	5.0	5.3
Benzo[a]fluorene	76.4	160.5	311.7	281.0	177.3	103.2	343.9
Benzo[b]fluorene	43.2	83.9	168.8	141.3	103.8	64.7	211.9
B21T	128.6	225.9	443.7	293.0	169.4	138.1	292.2
Benzo[ghi]fluoranthene	158.3	306.1	691.4	592.5	296.3	168.3	411.1
Benzo[c]phenanthrene	49.3	70.3	194.8	112.2	61.5	53.1	155.4
B23T	23.0	48.9	110.2	57.8	35.1	53.4	117.8
Benz[a]anthracene	357.2	657.1	2219.5	979.8	469.6	950.0	2566.3
Cyclopenta[cd]pyrene	38.8	66.2	194.6	98.9	<0.2	<0.2	626.6
Chrysene	744.0	1063.2	3047.6	1576.2	469.5	<0.1	2997.9
Benzanthrone	57.6	115.6	296.4	169.1	92.1	195.3	571.9
2-Nitrofluoranthene	10.3	<0.9	<0.9	<0.9	11.0	12.3	18.6
B[a]A-7,12-dione	45.1	60.8	79.2	63.3	49.4	88.1	133.7
Benzo[b]fluoranthene	369.0	760.8	2048.0	1030.0	505.5	2394.3	4835.8
Benzo[k]fluoranthene	179.5	366.3	1196.8	409.7	230.9	1157.8	2658.8
Benzo[j]fluoranthene	168.0	416.0	1126.6	476.3	222.8	1110.8	2636.2
Benzo[e]pyrene	286.5	556.9	1813.7	693.5	403.4	1904.3	3837.8
Benzo[a]pyrene	212.5	493.6	1872.1	648.7	201.4	1481.2	4428.5
Perylene	56.0	108.6	444.6	147.0	55.8	457.5	1178.3
Indeno[1,2,3-cd]pyrene	219.9	474.5	1445.5	595.6	310.5	1999.6	4048.5
Dibenz[a,c]anthracene	26.9	62.9	174.2	214.1	83.4	430.4	905.0
Picene	30.8	57.7	213.4	84.0	47.5	345.6	690.4
Benzo[ghi]perylene	369.8	651.8	2087.0	1006.5	639.7	2378.6	4919.6
Coronene	197.3	384.7	840.8	723.4	520.8	823.9	1627.0
Dibenzo[a,e]pyrene	32.6	53.4	233.7	74.2	52.1	303.1	738.8
Dibenzo[a,i]pyrene	27.9	45.1	229.0	72.1	42.3	371.9	860.9
Dibenzo[a,h]pyrene	12.6	18.8	94.7	35.6	17.9	190.5	456.5
Thiacoronene	31.4	66.8	123.0	185.8	156.4	75.2	141.5
% Recovery d10-phen.	79	84	88	58	126	68	61
% Recovery d12-Chrysene	97	104	93	89	124	123	113
% Recovery d14-DB[a,h]A	66	70	63	55	98	109	88
Total PAC (ng/m3)	7.3	13.4	31.2	19.5	12.1	19.2	46.5
R234	4.6	4.6	3.3	4.3	4.4	2.5	2.0
R234 Classification	P	P	P	P	P	C	C

* to translate to ng/g, multiply values by Volume of air (m3), then divide by Mass Particulate (g)

* NR=not reported (L.M.Allan), C=coke oven designation, P=petrogenic designation, n/a=rec. standard not used

Date Collected	July 17/95	July 18/95	July 19/95	July 20/95	July 23/95	July 29/95	Aug. 2/95
Sampling Site	Gertrude	Gertrude	Gertrude	Gertrude	Gertrude	Gertrude	Philip
GC-MS Data File	GERJL17D	GERJL18D	GERJL19D	GERJL20D	GERJL23D	GERJL29D	PHLAG02D
Volume of Air (m3)	1620	1620	1620	1620	1620	1620	1434
Mass Particulate (g)	0.039	0.055	0.046	0.044	0.031	0.041	0.063
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	DCM	DCM
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	<0.09	<0.09	0.9	NR	NR	NR	1.6
Phenanthrene	4.2	5.0	26.3	NR	NR	NR	44.9
Anthracene	0.3	0.6	2.2	NR	NR	NR	4.9
o-Terphenyl	0.2	0.2	0.8	NR	NR	NR	0.6
1-Methylphenanthrene	3.4	4.2	7.4	NR	NR	NR	37.1
Anthraquinone	13.2	15.3	19.4	NR	NR	NR	98.0
Fluoranthene	134.3	177.4	231.8	NR	NR	NR	1275.1
Pyrene	120.1	166.9	214.7	NR	NR	NR	1662.7
m-Terphenyl	1.6	1.4	2.2	NR	NR	NR	11.8
p-Terphenyl	1.1	1.1	1.3	NR	NR	NR	7.6
Benzo[a]fluorene	11.3	12.9	26.6	NR	NR	NR	59.6
Benzo[b]fluorene	5.5	6.7	14.8	NR	NR	NR	30.5
B21T	17.0	16.1	27.4	7.8	4.0	11.7	76.5
Benzo[ghi]fluoranthene	21.2	21.9	36.4	13.1	7.0	17.9	412.2
Benzo[c]phenanthrene	8.1	8.6	15.1	5.3	3.3	6.5	41.0
B23T	3.9	3.4	8.4	NR	NR	NR	12.6
Benz[a]anthracene	63.7	63.2	158.8	28.3	15.1	32.8	161.7
Cyclopenta[cd]pyrene	2.5	3.8	8.7	6.5	4.2	6.8	25.4
Chrysene	155.0	127.7	228.4	66.8	30.7	77.1	335.9
Benzanthrone	18.7	17.6	27.9	NR	NR	NR	53.5
2-Nitrofluoranthene	2.5	1.9	1.7	NR	NR	NR	1.3
B[a]A-7,12-dione	18.0	13.9	16.7	NR	NR	NR	10.6
Benzo[b]fluoranthene	117.9	105.0	209.1	71.5	66.8	126.7	133.1
Benzo[k]fluoranthene	50.9	47.7	114.5	34.2	23.2	45.6	53.7
Benzo[j]fluoranthene	49.9	46.3	110.3	37.7	26.6	54.9	61.3
Benzo[e]pyrene	86.5	86.7	162.7	62.3	56.5	146.9	126.1
Benzo[a]pyrene	43.9	51.5	133.7	47.8	26.0	58.0	48.7
Perylene	10.3	12.0	30.7	10.9	6.2	12.3	10.4
Indeno[1,2,3-cd]pyrene	74.6	81.9	178.4	101.1	90.9	133.9	113.9
Dibenz[a,c]anthracene	15.8	15.4	41.9	6.5	8.9	16.5	34.5
Picene	9.5	9.9	29.7	NR	NR	NR	5.8
Benzo[ghi]perylene	128.5	146.0	219.3	108.1	91.2	190.0	456.6
Coronene	81.4	88.5	98.1	73.1	65.1	112.4	443.2
Dibenzo[a,e]pyrene	11.1	13.0	30.6	NR	NR	NR	19.9
Dibenzo[a,i]pyrene	10.2	11.6	33.2	NR	NR	NR	5.2
Dibenzo[a,h]pyrene	2.6	4.0	9.9	NR	NR	NR	1.4
Thiacoronene	2.7	2.8	3.8	NR	NR	NR	108.3
% Recovery d10-phen.	5	4	27	78	70	76	8
% Recovery d12-Chrysene	82	77	79	84	81	92	71
% Recovery d14-DB[a,h]A	79	74	75	82	79	88	59
Total PAC (ng/m3)	1.3	1.4	2.5	0.7	0.5	1.1	5.9
R234	3.6	3.3	2.7	4.2	3.8	3.5	5.7
R234 Classification	P	P	C	P	P	P	P

Date Collected	Aug. 2/95	Aug. 15/95	Aug. 15/95	Apr. 12/96	Apr. 14/96	Apr. 10/96	Apr. 16/96
Sampling Site	Gertrude	Philip	Gertrude	Pier 25	Pier 25	Pier 25	Pier 25
GC-MS Data File	GERAG02D	PHLAG15D	GERAG15D	25AP12DA	25AP14DA	25AP10DA	25AP16DA
Volume of Air (m3)	1849	1434	1620	1627	1631	1631	1631
Mass Particulate (g)	0.148	0.202	0.055	0.021	0.014	0.142	0.054
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	DCM	DCM
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	30.5	85.5	NR	1.3	2.8	91.9	48.8
Phenanthrene	601.6	932.3	NR	22.7	44.6	1945.1	745.8
Anthracene	89.9	63.8	NR	1.5	3.6	493.8	185.6
o-Terphenyl	2.1	2.9	NR	0.4	0.8	3.1	1.2
1-Methylphenanthrene	73.8	118.5	NR	4.4	7.9	221.1	115.3
Anthraquinone	114.8	203.1	NR	52.4	70.4	506.0	209.1
Fluoranthene	814.7	1682.6	NR	9.6	132.6	6370.1	3061.7
Pyrene	691.4	1854.4	NR	999.2	13650.8	6431.4	2853.2
m-Terphenyl	6.3	25.1	NR	0.7	1.1	16.2	6.3
p-Terphenyl	3.6	14.3	NR	0.5	0.9	12.1	4.5
Benzo[a]fluorene	142.2	134.6	NR	19.2	18.4	1347.3	591.4
Benzo[b]fluorene	93.0	77.4	NR	15.9	14.8	988.2	255.3
B21T	134.8	377.9	17.9	17.5	17.0	1629.5	503.7
Benzo[ghi]fluoranthene	158.0	461.4	29.7	19.7	27.4	2487.0	646.0
Benzo[c]phenanthrene	68.9	115.8	11.7	8.7	12.1	1282.0	352.3
B23T	58.0	110.4	NR	4.0	3.4	568.1	205.2
Benz[a]anthracene	1204.8	1985.5	108.1	109.9	119.2	17521.4	4084.1
Cyclopenta[cd]pyrene	95.0	91.5	25.1	4.1	14.6	2614.1	956.5
Chrysene	1587.8	2891.2	166.7	152.2	145.8	22599.0	6001.1
Benzanthrone	247.8	200.9	NR	266.6	107.6	2634.6	13.6
2-Nitrofluoranthene	<0.9	21.8	NR	2.9	35.5	36.7	26.2
B[a]A-7,12-dione	106.1	81.4	NR	27.4	55.2	784.8	423.2
Benzo[b]fluoranthene	3843.4	1941.3	281.0	295.3	161.0	28068.1	7595.5
Benzo[k]fluoranthene	1901.8	928.6	118.0	89.7	51.1	13798.4	1797.0
Benzo[j]fluoranthene	1822.0	881.7	128.0	74.7	53.7	13610.8	3727.8
Benzo[e]pyrene	3055.8	1626.9	228.7	204.6	109.7	22549.8	6117.1
Benzo[a]pyrene	2524.6	1348.4	183.5	69.4	44.8	26365.2	5097.5
Perylene	663.0	359.9	49.1	10.0	11.3	6979.9	1564.2
Indeno[1,2,3-cd]pyrene	3009.5	1517.3	609.7	84.0	64.9	19504.4	4105.0
Dibenz[a,c]anthracene	755.8	182.9	33.2	10.4	8.0	1612.7	775.2
Picene	579.6	202.3	NR	34.3	16.6	4393.3	<0.2
Benzo[ghi]perylene	3052.6	2052.3	351.2	136.6	104.9	21835.5	6047.4
Coronene	721.5	608.2	228.5	42.3	52.3	5078.8	1990.8
Dibenzo[a,e]pyrene	542.9	188.2	NR	14.2	8.2	3229.3	1024.0
Dibenzo[a,i]pyrene	661.5	201.5	NR	2.3	4.7	3924.1	883.2
Dibenzo[a,h]pyrene	334.3	77.6	NR	0.3	0.5	676.8	110.9
Thiacoronene	32.7	68.3	NR	0.6	1.5	438.7	129.7
% Recovery d10-phen.	128	121	n/a	n/a	n/a	n/a	n/a
% Recovery d12-Chrysene	97	68	n/a	n/a	n/a	n/a	n/a
% Recovery d14-DB[a,h]A	85	66	n/a	n/a	n/a	n/a	n/a
Total PAC (ng/m3)	29.8	23.6	2.6	2.8	15.2	242.2	62.1
R234	1.9	3.2	3.3	4.4	4.1	2.0	2.5
R234 Classification	C	P	P	P	P	C	C

Date Collected	Apr. 20/96	Apr. 23/96	Apr. 26/96	May 1/96	May 12/96	May 13/96	Sept. 4/97
Sampling Site	Pier 25	Pier 25	Pier 25	Pier 25	Pier 25	Pier 25	Pool
GC-MS Data File	25AP20DA	25AP23DA	25AP26DA	25MY01DA	25MY12DA	25MY13DA	POLSE04D
Volume of Air (m3)	1631	1637	1630	1632	1632	1639	1684
Mass Particulate (g)	0.058	0.034	0.083	0.054	0.042	0.082	0.085
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	DCM	DCM
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	31.3	31.4	81.4	32.1	13.4	59.3	19.3
Phenanthrene	891.1	873.6	1937.2	806.9	331.0	701.5	287.8
Anthracene	288.8	153.5	500.8	213.9	103.2	735.0	55.2
o-Terphenyl	2.0	2.6	2.9	0.7	1.0	0.6	1.2
1-Methylphenanthrene	171.8	112.4	223.3	69.6	51.4	165.2	38.6
Anthraquinone	258.6	271.9	614.1	184.3	162.6	372.2	141.1
Fluoranthene	6413.0	3351.8	7252.4	2431.3	1384.1	4964.7	976.0
Pyrene	5620.5	2959.2	6554.8	2176.6	1385.1	4830.9	780.2
m-Terphenyl	12.5	7.9	14.3	37.0	3.0	10.9	3.8
p-Terphenyl	9.0	5.4	10.8	2.0	1.8	6.9	2.7
Benzo[a]fluorene	1665.3	608.1	1377.7	363.8	236.0	101.6	89.1
Benzo[b]fluorene	1045.5	483.6	970.6	244.3	129.4	749.7	55.0
B21T	1176.8	525.2	1148.3	270.7	150.0	807.7	130.9
Benzo[ghi]fluoranthene	1115.0	620.1	1478.5	384.7	240.8	980.0	147.6
Benzo[c]phenanthrene	728.3	327.0	843.0	214.8	120.9	608.2	50.7
B23T	474.0	230.4	458.8	82.6	63.5	357.9	56.4
Benz[a]anthracene	9084.7	4158.1	9702.4	2550.9	1605.7	8812.9	1005.5
Cyclopenta[cd]pyrene	1823.4	987.7	1928.2	502.0	518.8	1380.9	73.3
Chrysene	11069.3	6060.3	12868.2	3253.8	2171.5	11229.7	1241.9
Benzanthrone	23.5	1348.4	183.8	5.1	9.8	2288.9	309.9
2-Nitrofluoranthene	58.7	34.4	59.9	6.1	1.6	78.9	8.2
B[a]A-7,12-dione	539.7	838.5	928.2	414.2	249.5	588.5	55.8
Benzo[b]fluoranthene	16151.8	8272.1	15891.5	5108.1	3570.6	13305.7	1572.5
Benzo[k]fluoranthene	5265.1	4064.4	6961.9	1917.9	1160.8	7828.4	872.3
Benzo[j]fluoranthene	7892.1	3942.3	7891.6	2625.5	1818.3	7492.6	815.4
Benzo[e]pyrene	12334.8	6289.4	12295.1	4056.8	2993.8	10483.2	1265.8
Benzo[a]pyrene	14176.0	6231.5	12473.2	4508.1	3026.2	13118.6	1337.4
Perylene	3981.7	1912.8	3382.1	1294.4	859.2	3383.7	365.8
Indeno(1,2,3-cd)pyrene	10895.4	5994.8	11030.2	3881.5	2744.5	8481.1	1304.6
Dibenz[a,c]anthracene	2037.5	867.9	929.8	582.9	358.0	1299.1	187.4
Picene	<0.2	1636.0	90.4	<0.2	<0.2	2378.7	220.1
Benzo[ghi]perylene	10267.1	1201.7	11547.9	3890.7	3061.9	8357.8	1428.2
Coronene	2246.5	1313.6	2648.2	973.8	753.5	1503.1	496.5
Dibenzo[a,e]pyrene	2488.0	1176.5	1791.3	738.1	459.3	1526.3	230.5
Dibenzo[a,i]pyrene	2593.3	1439.2	1551.9	709.0	378.2	2415.6	267.1
Dibenzo[a,h]pyrene	532.0	267.3	358.5	140.3	70.5	386.3	180.5
Thiacoronene	106.9	76.7	151.5	49.6	47.7	73.1	30.1
% Recovery d10-phen.	n/a	n/a	n/a	n/a	n/a	n/a	90
% Recovery d12-Chrysene	n/a	n/a	n/a	n/a	n/a	n/a	96
% Recovery d14-DB[a,h]A	n/a	n/a	n/a	n/a	n/a	n/a	87
Total PAC (ng/m3)	133.4	68.6	138.0	44.7	30.2	121.8	16.1
R234	2.5	2.3	2.6	2.4	2.4	2.3	2.2
R234 Classification	C	C	C	C	C	C	C

Date Collected	Sept. 9/97	Sept. 10/97	Sept. 22/97	Sept. 29/97	Sept. 4/97	Sept. 9/97	Sept. 10/97
Sampling Site	Dofasco 1	Pool	Pool	Pool	Dofasco 1	Pool	Dofasco 1
GC-MS Data File	DOFSE09D	POLSE10D	POLSE22D	POLSE29D	DOFSE04D	POLSE09D	DOFSE10D
Volume of Air (m3)	1634	1797	1382	3035	1674	1642	1833
Mass Particulate (g)	0.053	0.054	0.062	0.066	0.063	0.039	0.031
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	DCM	DCM
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	1.6	<0.09	3.1	9.5	1.4	<0.09	0.4
Phenanthrene	30.3	9.8	59.6	160.4	31.4	3.4	5.9
Anthracene	4.7	1.8	10.4	27.1	4.2	0.6	0.8
o-Terphenyl	0.3	0.2	0.8	0.5	0.5	0.3	0.2
1-Methylphenanthrene	9.0	8.2	12.9	19.3	13.9	1.7	3.3
Anthraquinone	41.1	34.6	35.5	32.4	77.9	15.2	18.8
Fluoranthene	178.7	209.8	412.7	456.5	604.5	69.3	86.4
Pyrene	190.5	211.3	353.1	406.3	415.2	60.1	79.1
m-Terphenyl	1.0	2.1	1.5	1.9	1.9	0.8	1.2
p-Terphenyl	0.7	1.6	1.8	1.6	1.3	0.4	0.7
Benzo[a]fluorene	8.6	18.3	40.6	49.7	47.7	9.0	5.2
Benzo[b]fluorene	5.2	11.5	23.7	32.6	27.4	2.3	2.9
B21T	39.5	46.9	87.3	84.6	65.0	9.7	23.3
Benzo[ghi]fluoranthene	48.2	117.3	128.7	103.7	78.3	12.9	32.9
Benzo[c]phenanthrene	8.9	16.2	32.2	31.8	27.5	3.3	5.4
B23T	7.7	10.1	26.5	28.6	14.5	1.7	3.9
Benz[a]anthracene	103.6	181.3	615.1	656.7	347.4	23.5	50.8
Cyclopenta[cd]pyrene	14.1	28.2	41.3	64.3	23.1	5.0	7.1
Chrysene	312.5	350.4	806.5	863.1	498.1	73.9	166.8
Benzanthrone	160.3	362.3	105.8	119.6	118.7	89.8	118.6
2-Nitrofluoranthene	4.9	3.1	6.9	2.3	2.0	0.7	1.1
B[a]A-7,12-dione	32.9	20.6	26.9	37.4	25.8	10.3	14.1
Benzo[b]fluoranthene	288.9	174.9	611.8	883.9	360.3	108.0	69.9
Benzo[k]fluoranthene	105.6	81.9	330.8	469.9	196.1	32.6	29.3
Benzo[j]fluoranthene	100.9	81.1	306.3	429.2	175.5	28.7	28.1
Benzo[e]pyrene	217.1	143.6	490.7	713.3	314.6	80.9	56.9
Benzo[a]pyrene	102.7	113.0	525.8	636.9	232.2	30.3	27.9
Perylene	18.6	25.1	133.2	183.4	59.4	5.1	6.3
Indeno[1,2,3-cd]pyrene	156.9	123.2	495.0	744.0	350.6	52.4	48.4
Dibenz[a,c]anthracene	<0.2	8.2	<0.2	89.1	41.5	4.7	4.5
Picene	14.3	12.1	74.7	111.4	50.2	5.4	4.2
Benzo[ghi]perylene	234.5	231.7	627.9	881.5	627.2	64.9	96.0
Coronene	95.4	118.8	243.1	291.1	346.8	19.4	62.0
Dibenzo[a,e]pyrene	12.6	16.0	79.1	115.5	57.8	3.8	5.7
Dibenzo[a,i]pyrene	6.0	6.0	84.3	82.9	54.5	3.4	4.2
Dibenzo[a,h]pyrene	<0.4	5.1	45.9	7.5	32.0	<0.4	1.2
Thiacoronene	2.9	5.6	13.6	18.1	9.4	0.7	1.7
% Recovery d10-phen.	32	8	35	92	19	11	9
% Recovery d12-Chrysene	105	94	88	90	94	105	89
% Recovery d14-DB[a,h]A	72	83	90	88	83	71	79
Total PAC (ng/m3)	2.6	2.8	6.9	8.8	5.3	0.8	1.1
R234	4.8	3.9	2.8	2.5	3.2	4.2	5.1
R234 Classification	P	P	C	C	P	P	P

Date Collected	Sept. 22/97	Sept. 29/97	May 8/98	May 9/98	May 10/98	May 11/98	May 13/98
Sampling Site	Dofasco 1	Dofasco 1	Dofasco 2	Dofasco 2	Dofasco 2	Dofasco 2	Dofasco 2
GC-MS Data File	DOFSE22D	DOFSE29D	DOFMY08D	DOFMY09D	DOFMY10D	DOFMY11D	DOFMY13D
Volume of Air (m3)	1468	3067	1630	1587	1652	1598	1623
Mass Particulate (g)	0.024	0.101	0.088	0.026	0.009	0.013	0.173
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	DCM	DCM
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	10.2	15.3	7.6	<0.09	<0.09	0.7	75.8
Phenanthrene	84.7	243.2	267.5	0.5	13.7	49.2	3097.2
Anthracene	10.6	39.5	10.7	<0.1	<0.1	4.6	211.5
o-Terphenyl	1.2	0.6	0.7	<0.2	0.5	0.4	<0.2
1-Methylphenanthrene	17.7	24.0	27.1	0.8	3.3	9.5	324.2
Anthraquinone	34.5	31.7	104.7	12.7	17.2	34.6	612.5
Fluoranthene	326.6	551.3	1137.9	106.6	147.0	384.1	13569.3
Pyrene	276.4	491.0	946.8	113.7	109.6	309.4	11056.1
m-Terphenyl	2.5	2.0	3.2	0.9	1.0	1.5	22.1
p-Terphenyl	2.1	1.3	2.1	0.8	0.7	1.1	13.3
Benzo[a]fluorene	22.2	60.7	76.2	13.9	5.3	25.9	1237.6
Benzo[b]fluorene	12.1	37.9	48.0	8.0	2.2	12.9	693.3
B21T	45.5	102.4	164.4	36.4	15.7	45.4	1165.5
Benzo[ghi]fluoranthene	83.3	116.2	159.4	50.9	24.7	49.5	1142.1
Benzo[c]phenanthrene	18.0	45.4	64.8	11.8	5.4	15.2	677.8
B23T	8.5	47.9	36.0	7.5	1.6	7.0	410.0
Benz[a]anthracene	197.8	853.5	841.2	135.0	43.1	205.8	6474.8
Cyclopenta[cd]pyrene	10.1	76.3	12.4	2.9	<0.2	<0.2	55.5
Chrysene	392.0	1073.0	1214.1	229.5	124.6	327.1	8052.5
Benzanthrone	93.6	220.6	66.5	25.8	14.2	29.3	149.0
2-Nitrofluoranthene	5.9	<0.9	4.9	<0.9	0.1	0.9	
B[a]A-7,12-dione	20.4	53.1	42.9	14.4	8.3	13.6	153.4
Benzo[b]fluoranthene	196.9	1512.4	641.2	185.7	93.5	206.7	3927.1
Benzo[k]fluoranthene	91.7	940.7	319.9	76.4	29.3	91.9	2106.8
Benzo[j]fluoranthene	101.8	831.5	297.6	73.6	28.5	79.0	1939.2
Benzo[e]pyrene	150.7	1325.0	473.3	138.7	64.2	150.6	3006.6
Benzo[a]pyrene	123.8	1285.1	472.6	67.4	10.9	78.2	3493.2
Perylene	25.0	409.9	115.5	11.5	1.7	17.2	931.2
Indeno[1,2,3-cd]pyrene	170.6	1579.2	457.8	102.9	48.1	69.7	3622.3
Dibenz[a,c]anthracene	15.5	296.7	<0.2	2.4	1.1	<0.2	852.1
Picene	20.8	272.6	69.5	13.6	7.5	20.9	610.0
Benzo[ghi]perylene	248.8	1681.6	506.7	175.3	70.6	145.3	3701.8
Coronene	129.0	513.1	147.1	72.3	38.1	50.9	1071.9
Dibenzo[a,e]pyrene	23.4	331.8	66.6	12.5	4.7	17.3	793.1
Dibenzo[a,i]pyrene	23.2	307.1	79.2	14.2	6.0	19.0	957.8
Dibenzo[a,h]pyrene	6.7	192.3	28.9	<0.4	<0.4	2.5	524.5
Thiacoronene	4.2	21.9	10.1	6.0	1.3	2.1	58.0
% Recovery d10-phen.	69	109	77	1	28	49	77
% Recovery d12-Chrysene	88	84	78	72	69	70	70
% Recovery d14-DB[a,h]A	87	82	75	73	76	75	74
Total PAC (ng/m3)	3.0	15.6	8.9	1.7	0.9	2.5	76.7
R234	4.4	2.1	3.9	4.6	7.7	4.6	2.8
R234 Classification	P	C	P	P	P	P	C

Date Collected	May 30/98	June 9/98	June 11/98	June 12/98	June 23/98	June 29/98	July 6/98
Sampling Site	Dofasco 2	Dofasco 2	Dofasco 2	Pool	Dofasco 2	Pool	Dofasco 2
GC-MS Data File	DOFMY30D	DOFJN09D	DOFJN11D	POLJN12D	DOFJN23D	POLJN29D	DOFJL06D
Volume of Air (m3)	1624	1722	1600	1674	1570	1700	1638
Mass Particulate (g)	0.050	0.059	0.060	0.048	0.083	0.110	0.043
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	DCM	DCM
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	<0.09	7.2	<0.09	<0.09	0.9	2.5	<0.09
Phenanthrene	1.3	201.6	16.4	73.6	36.7	96.2	1.9
Anthracene	0.2	201.6	3.3	8.6	2.1	<0.1	0.3
o-Terphenyl	<0.2	1.0	<0.2	0.3	<0.2	0.5	<0.2
1-Methylphenanthrene	2.0	21.9	3.6	11.6	9.9	15.6	2.2
Anthraquinone	29.4	69.7	25.0	33.0	80.4	56.3	19.9
Fluoranthene	274.3	587.8	206.2	235.3	368.2	497.3	137.2
Pyrene	263.3	466.6	179.2	199.6	329.0	417.7	125.7
m-Terphenyl	0.6	2.8	0.2	1.7	0.8	2.1	1.1
p-Terphenyl	0.7	1.7	0.2	1.5	0.5	1.4	0.8
Benzo[a]fluorene	34.0	43.9	10.9	22.0	20.1	42.1	13.2
Benzo[b]fluorene	19.3	21.2	5.9	12.5	12.1	25.5	8.1
B21T	56.2	87.5	37.1	57.9	80.3	79.7	40.5
Benzo[ghi]fluoranthene	58.6	94.5	49.1	70.4	122.7	86.9	45.1
Benzo[c]phenanthrene	24.4	30.3	11.4	15.9	24.7	26.5	11.5
B23T	13.0	17.5	6.6	11.8	10.1	14.1	6.4
Benz[a]anthracene	250.9	374.0	144.5	205.1	251.2	402.3	114.2
Cyclopenta[cd]pyrene	<0.2	<0.2	5.5	2.0	4.3		0.1
Chrysene	453.0	633.5	291.1	403.1	669.2	662.9	292.4
Benzanthrone	40.0	48.5	22.5	34.9	59.7	41.5	26.4
2-Nitrofluoranthene	2.5	5.4	1.4	4.3	13.8	5.0	1.9
B[a]A-7,12-dione	39.5	35.9	11.9	18.9	44.2	31.1	23.5
Benzo[b]fluoranthene	302.9	271.6	103.7	152.1	282.2	442.4	156.6
Benzo[k]fluoranthene	161.6	199.8	49.5	77.3	126.8	221.5	67.9
Benzo[j]fluoranthene	146.9	150.3	46.9	70.4	126.8	206.0	66.1
Benzo[e]pyrene	220.4	216.0	82.1	108.5	209.3	325.3	108.3
Benzo[a]pyrene	140.2	204.0	66.2	81.0	80.9	231.6	33.5
Perylene	31.0	39.3	15.1	18.2	19.5	62.4	9.8
Indeno[1,2,3-cd]pyrene	56.4	47.3	27.3	46.7	121.6	126.3	66.4
Dibenz[a,c]anthracene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Picene	30.9	30.7	12.2	14.1	23.7	49.1	11.1
Benzo[ghi]perylene	206.7	264.6	95.9	134.5	260.6	349.8	129.5
Coronene	74.6	107.4	38.5	62.3	122.3	114.9	61.8
Dibenzo[a,e]pyrene	24.8	34.8	13.5	16.3	20.5	51.3	9.4
Dibenzo[a,i]pyrene	28.9	43.7	13.6	16.9	20.4	58.4	10.0
Dibenzo[a,h]pyrene	<0.4	16.5	7.1	7.0	<0.4	9.3	<0.4
Thiacoronene	6.5	6.9	2.0	4.8	6.1	7.9	3.7
% Recovery d10-phen.	1	97	17	67	21	51	2
% Recovery d12-Chrysene	68	68	65	66	69	67	76
% Recovery d14-DB[a,h]A	66	65	65	72	65	66	73
Total PAC (ng/m3)	3.0	4.6	1.6	2.2	3.6	4.8	1.6
R234	3.8	4.4	4.4	5.0	6.9	4.4	5.1
R234 Classification	P	P	P	P	P	P	P

Date Collected	May 8/98	May 9/98	May 10/98	May 11/98	May 13/98	May 30/98	June 9/98
Sampling Site	Pool	Pool	Pool	Pool	Pool	Pool	Pool
GC-MS Data File	POLMY08D	POLMY09D	POLMY10D	POLMY11D	POLMY13D	POLMY30D	POLJN09D
Volume of Air (m3)	1629	1588	1661	1536	1626	1632	1438
Mass Particulate (g)	0.036	0.014	0.007	0.006	0.044	0.036	0.020
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	DCM	DCM
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	1.1	<0.09	<0.09	<0.09	<0.09	0.5	<0.09
Phenanthrene	32.4	0.7	<0.1	0.9	16.1	24.8	8.2
Anthracene	32.4	<0.1	<0.1	<0.1	2.5	0.9	<0.1
o-Terphenyl	0.3	<0.2	<0.2	<0.2	0.3	0.6	0.3
1-Methylphenanthrene	4.8	<0.2	<0.2	<0.2	10.4	5.4	3.7
Anthraquinone	15.7	3.0	3.0	4.6	61.9	15.1	19.0
Fluoranthene	125.0	31.4	23.9	55.4	585.3	179.3	165.2
Pyrene	95.3	28.9	18.0	50.5	496.2	150.5	133.3
m-Terphenyl	1.0	0.5	0.4	0.4	3.2	1.1	1.1
p-Terphenyl	0.6	0.3	0.2	<0.2	1.8	0.6	0.6
Benzo[a]fluorene	7.7	2.6	1.0	4.4	68.1	14.1	10.1
Benzo[b]fluorene	3.6	1.3	0.5	1.5	35.3	6.9	5.3
B21T	16.6	8.6	2.6	7.8	107.9	22.5	20.7
Benzo[ghi]fluoranthene	20.5	8.0	2.9	10.2	149.5	24.5	25.2
Benzo[c]phenanthrene	6.5	2.9	0.8	2.8	42.9	9.5	8.1
B23T	2.2	1.3	0.7	1.1	26.5	4.3	3.5
Benz[a]anthracene	71.4	23.8	6.2	28.9	533.9	110.4	49.4
Cyclopenta[cd]pyrene		0.5	0.1		27.6	2.8	1.8
Chrysene	133.0	57.1	26.4	53.0	695.1	161.6	159.7
Benzanthrone	14.8	4.3	1.7	2.6	50.3	9.5	19.7
2-Nitrofluoranthene	1.3	<0.9	<0.9	<0.9	9.5	<0.9	0.4
B[a]A-7,12-dione	6.7	1.2	1.2	1.6	21.2	4.8	10.6
Benzo[b]fluoranthene	24.1	46.6	23.0	36.2	196.0	53.6	105.1
Benzo[k]fluoranthene	59.4	8.3	4.5	7.3	101.5	26.8	49.5
Benzo[j]fluoranthene	24.3	6.4	4.0	5.9	97.9	24.3	45.1
Benzo[e]pyrene	41.4	31.0	16.7	24.3	162.2	40.2	82.4
Benzo[a]pyrene	21.1	4.7	1.4	2.6	146.7	37.0	57.8
Perylene	3.8	0.6	0.6	0.7	31.2	7.7	7.5
Indeno[1,2,3-cd]pyrene	20.2	23.2	20.0	20.7	149.5	47.6	108.0
Dibenz[a,c]anthracene	<0.2	0.5	0.6	0.5	3.9	1.6	2.9
Picene	5.0	3.8	4.0	4.5	18.4	7.1	13.6
Benzo[ghi]perylene	45.3	26.6	23.9	26.6	261.1	57.3	121.0
Coronene	21.3	10.7	8.3	9.5	130.1	27.2	47.6
Dibenzo[a,e]pyrene	4.4	2.8	2.3	2.2	21.7	7.4	15.4
Dibenzo[a,i]pyrene	4.9	3.5	3.3	3.5	20.5	7.7	16.9
Dibenzo[a,h]pyrene	0.8	<0.4	<0.4	<0.4	3.7	<0.4	1.9
Thiacoronene	0.7	0.3	0.2	0.2	7.1	1.7	2.0
% Recovery d10-phen.	52	2	1	1	9	52	14
% Recovery d12-Chrysene	69	73	69	76	72	77	74
% Recovery d14-DB[a,h]A	75	80	76	83	79	85	80
Total PAC (ng/m3)	0.9	0.3	0.2	0.4	4.3	1.1	1.3
R234	5.2	6.1	6.2	6.0	3.8	4.2	5.1
R234 Classification	P	P	P	P	P	P	P

Date Collected	June 11/98	June 12/98	June 23/98	June 29/98	July 6/98	
Sampling Site	Pool	Dofasco 2	Pool	Dofasco 2	Pool	
GC-MS Data File	POLJN11D	DOFJN12D	POLJN23D	DOFJN29D	POLJL06D	
Volume of Air (m3)	1606	1670	1569	1680	1639	DETECTION
Mass Particulate (g)	0.028	0.070	0.062	0.109	0.017	LIMIT
Extracting Solvent:	DCM	DCM	DCM	DCM	DCM	(PG/M3)
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	
Dibenzothiophene	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Phenanthrene	12.1	2.2	15.8	8.6	1.1	<0.1
Anthracene	1.9	1.1	15.9	<0.1	1.1	<0.1
o-Terphenyl	0.2	<0.2	0.2	<0.2	<0.2	<0.2
1-Methylphenanthrene	3.4	2.5	11.8	10.3	0.9	<0.2
Anthraquinone	11.2	30.1	67.4	70.5	4.7	<0.5
Fluoranthene	92.3	246.0	334.0	599.6	42.5	<0.1
Pyrene	76.5	222.2	280.6	506.1	38.6	<0.1
m-Terphenyl	0.9	0.5	3.2	1.6	0.5	<0.2
p-Terphenyl	0.5	0.5	1.7	1.9	0.3	<0.2
Benzo[a]fluorene	7.0	24.8	28.3	54.4	3.2	<0.2
Benzo[b]fluorene	3.0	14.9	17.5	27.4	1.3	<0.2
B21T	14.9	108.2	64.1	133.2	9.9	<0.1
Benzo[ghi]fluoranthene	21.2	100.8	112.8	130.1	9.2	<0.1
Benzo[c]phenanthrene	4.9	28.5	18.9	38.9	2.9	<0.2
B23T	1.8	19.4	8.4	<0.1	110.1	<0.1
Benz[a]anthracene	51.2	326.7	178.8	527.7	13.2	<0.1
Cyclopenta[cd]pyrene	1.4	2.5	8.6	<0.2	1.0	<0.2
Chrysene	111.0	845.2	436.1	1022.8	67.4	<0.1
Benzanthrone	9.4	40.2	44.8	55.4	5.1	<0.3
2-Nitrofluoranthene	0.5	5.8	10.7	6.5	0.4	<0.9
B[a]A-7,12-dione	4.6	39.1	33.5	52.4	4.8	<0.5
Benzo[b]fluoranthene	44.3	256.4	191.2	435.3	38.1	<0.2
Benzo[k]fluoranthene	23.0	119.6	88.4	296.0	12.5	<0.1
Benzo[j]fluoranthene	21.5	110.4	85.8	241.7	9.4	<0.1
Benzo[e]pyrene	33.1	171.1	146.5	348.1	26.7	<0.1
Benzo[a]pyrene	31.3	118.5	62.9	255.9	9.6	<0.2
Perylene	5.6	29.5	15.3	66.4	1.7	<0.2
Indeno[1,2,3-cd]pyrene	29.4	57.9	119.9	76.1	20.8	<0.2
Dibenz[a,c]anthracene	<0.2	<0.2	2.9	<0.2	<0.2	<0.2
Picene	4.6	22.4	16.1	55.0	2.9	<0.2
Benzo[ghi]perylene	45.0	194.6	184.8	379.1	24.6	<0.2
Coronene	18.8	84.7	94.1	128.9	11.8	<0.2
Dibenzo[a,e]pyrene	4.8	26.3	15.2	71.7	2.4	<0.2
Dibenzo[a,i]pyrene	4.5	17.8	14.4	68.1	2.8	<0.3
Dibenzo[a,h]pyrene	<0.4	14.2	<0.4	13.4	<0.4	<0.4
Thiacoronene	0.5	7.4	3.1	10.2	0.5	<0.06
% Recovery d10-phen.	24	1	11	3	2	
% Recovery d12-Chrysene	69	70	75	65	69	
% Recovery d14-DB[a,h]A	74	69	78	62	76	
Total PAC (ng/m3)	0.7	3.3	2.7	5.7	0.5	
R234	5.1	5.1	5.8	5.4	5.0	
R234 Classification	P	P	P	P	P	

Appendix VI: PAC concentrations in subsequent toluene extracts of ambient air samples (pg/m3)

Date Collected	July 14/95	July 17/95	July 18/95	July 19/95	July 20/95	July 23/95	July 29/95	July 17/95
Sampling Site	Philip	Philip	Philip	Philip	Philip	Philip	Philip	Gertrude
GC-MS Data File	PHLJL14T	PHLJL17T	PHLJL18T	PHLJL19T	PHLJL20T	PHLJL23T	PHLJL29T	GERJL17T
Volume of Air (m3)	1637	1434	1433	1434	1434	1434	1434	1620
Mass Particulate (g)	0.119	0.122	0.225	0.138	0.180	0.055	0.073	0.039
Extracting Solvent:	TOL	TOL	TOL	TOL	TOL	TOL	TOL	TOL
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	1.6	0.8	1.1	2.2	2.0	3.1	<0.09	1.3
Phenanthrene	49.7	60.7	51.7	132.7	735.8	133.6	70.3	38.4
Anthracene	0.9	2.7	50.9	3.8	78.5	16.5	70.4	38.2
o-Terphenyl	0.2	0.2	0.4	0.3	0.4	0.6	0.5	4.3
1-Methylphenanthrene	5.0	4.1	10.5	8.2	151.9	24.6	3.6	1.2
Anthraquinone	22.5	26.3	81.5	35.8	17.0	18.6	30.5	74.2
Fluoranthene	97.1	68.3	186.6	160.5	122.0	142.4	39.8	9.6
Pyrene	73.1	0.6	19.6	27.8	290.1	231.2	2.5	8.8
m-Terphenyl	1.0	1.1	3.2	2.2	2.1	1.5	0.9	3.6
p-Terphenyl	0.7	1.2	4.1	2.1	1.3	1.2	1.0	2.4
Benzo[a]fluorene	3.1	0.6	4.6	3.0	30.8	9.0	2.4	0.8
Benzo[b]fluorene	1.4	0.1	1.5	0.8	26.0	6.4	0.8	1.0
B21T	7.4	3.8	9.4	5.6	4.0	8.9	7.8	1.0
Benzo[ghi]fluoranthene	13.4	15.0	45.4	49.3	9.5	26.7	15.3	<0.1
Benzo[c]phenanthrene	2.8	1.2	5.0	3.3	2.7	3.5	2.9	<0.2
B23T	<0.1	<0.1	<0.1	0.6	<0.1	<0.1	0.9	0.7
Benz[a]anthracene	8.8	<0.1	<0.1	<0.1	50.3	39.7	<0.1	1.7
Cyclopenta[cd]pyrene	<0.2	<0.2	<0.2	<0.2	5.5	7.1	<0.2	<0.2
Chrysene	42.9	29.9	105.7	65.0	50.4	39.8	65.8	9.4
Benzanthrone	3.9	4.2	15.9	8.5	14.8	9.0	154.2	1.3
2-Nitrofluoranthene	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
B[a]A-7,12-dione	5.7	6.9	23.1	12.5	4.8	5.3	98.3	1.3
Benzo[b]fluoranthene	19.4	17.4	55.8	46.8	72.7	44.8	310.0	3.4
Benzo[k]fluoranthene	9.7	1.3	9.9	9.6	39.8	24.5	32.7	1.0
Benzo[j]fluoranthene	8.2	0.5	9.4	8.9	33.7	20.7	26.3	0.9
Benzo[e]pyrene	12.1	2.1	19.2	18.4	71.6	32.9	84.5	1.8
Benzo[a]pyrene	<0.2	<0.2	<0.2	<0.2	32.3	20.2	<0.2	0.4
Perylene	0.3	<0.2	<0.2	<0.2	7.4	4.0	2.2	<0.2
Indeno[1,2,3-cd]pyrene	19.3	0.7	10.1	12.8	62.6	49.3	24.0	1.6
Dibenz[a,c]anthracene	2.1	1.9	5.9	5.0	7.2	8.4	14.3	0.8
Picene	4.4	3.4	11.5	8.9	12.8	10.5	51.8	0.3
Benzo[ghi]perylene	26.2	<0.2	2.4	5.1	115.1	86.5	2.4	3.4
Coronene	37.9	29.1	70.7	94.9	48.2	97.3	188.6	2.0
Dibenzo[a,e]pyrene	1.9	0.9	2.2	3.0	6.9	8.0	5.3	0.3
Dibenzo[a,i]pyrene	1.7	1.1	3.7	2.7	7.5	10.6	12.4	<0.2
Dibenzo[a,h]pyrene	<0.4	<0.4	<0.4	<0.4	<0.4	2.0	<0.4	<0.4
Thiacoronene	4.8	1.1	6.6	8.1	3.6	21.5	13.2	0.1
Total PAC (ng/m3)	0.48	0.29	0.82	0.74	2.12	1.15	1.32	0.22
R234 Classification (DCM)	P	P	P	P	P	C	C	P

* to translate to ng/g, multiply values by Volume of air (m3), then divide by Mass Particulate (g)

* C=coke oven designation, P=petrogenic designation

Date Collected	July 18/95	July 19/95	July 20/95	July 23/95	July 29/95	Aug. 2/95	Aug. 2/95	Aug. 15/95
Sampling Site	Gertrude	Gertrude	Gertrude	Gertrude	Gertrude	Philip	Gertrude	Philip
GC-MS Data File	GERJL18T	GERJL19T	GERJL20T	GERJL23T	GERJL29T	PHLAG02T	GERAG02T	PHLAG15T
Volume of Air (m3)	1620	1620	1620	1620	1620	1434	1849	1434
Mass Particulate (g)	0.055	0.046	0.044	0.031	0.041	0.063	0.148	0.202
Extracting Solvent:	TOL	TOL	TOL	TOL	TOL	TOL	TOL	TOL
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	<0.09	0.3	<0.09	<0.09	<0.09	<0.09	<0.09	4.6
Phenanthrene	33.1	8.3	6.4	4.3	27.0	457.7	106.5	65.4
Anthracene	42.5	2.6	1.3	0.5	4.3	495.7	36.5	2.1
o-Terphenyl	1.9	1.0	2.6	0.5	0.8	0.4	0.7	0.1
1-Methylphenanthrene	2.8	1.3	1.2	1.5	5.1	104.9	8.5	13.8
Anthraquinone	14.6	5.5	5.1	4.8	14.1	44.5	67.2	42.0
Fluoranthene	22.7	14.2	27.0	35.7	135.3	173.7	84.7	144.7
Pyrene	4.7	2.1	13.3	12.1	71.9	3.0	23.9	196.3
m-Terphenyl	1.4	0.9	0.6	0.6	0.8	2.2	2.5	3.0
p-Terphenyl	0.8	0.5	<0.2	<0.2	0.4	1.8	2.5	3.8
Benzo[a]fluorene	0.8	0.7	0.8	2.2	8.6	6.2	11.0	7.0
Benzo[b]fluorene	0.4	0.3	0.3	1.0	4.4	1.4	7.4	4.2
B21T	0.6	0.5	1.1	0.9	3.0	<0.1	4.1	21.0
Benzo[ghi]fluoranthene	1.7	1.6	2.1	1.6	3.2	49.2	11.4	32.9
Benzo[c]phenanthrene	0.5	0.5	0.6	0.5	1.2	1.9	6.3	5.6
B23T	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	5.1
Benz[a]anthracene	0.7	0.7	1.2	0.4	2.1	<0.1	5.0	77.2
Cyclopenta[cd]pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	5.3
Chrysene	13.0	9.6	8.3	4.8	10.7	41.7	170.5	150.2
Benzanthrone	2.4	1.9	1.0	0.9	1.6	11.5	85.7	13.6
2-Nitrofluoranthene	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	0.6
B[a]A-7,12-dione	2.5	1.7	1.0	1.0	1.6	6.3	41.7	7.5
Benzo[b]fluoranthene	6.4	5.5	2.4	2.5	3.5	24.8	271.8	74.2
Benzo[k]fluoranthene	0.9	0.8	0.7	0.5	1.2	1.5	97.1	44.8
Benzo[j]fluoranthene	0.9	0.9	0.9	0.6	1.2	1.1	93.1	37.2
Benzo[e]pyrene	2.2	2.1	1.5	1.4	2.8	5.7	152.1	52.4
Benzo[a]pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	52.0
Perylene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	8.6
Indeno[1,2,3-cd]pyrene	1.4	1.1	1.3	1.1	2.3	1.9	76.0	87.3
Dibenz[a,c]anthracene	1.2	0.8	0.4	0.4	0.6	5.3	<0.2	4.9
Picene	1.1	0.6	<0.2	0.3	0.5	2.9	36.0	18.5
Benzo[ghi]perylene	0.3	0.3	1.5	0.8	2.6	0.4	63.4	111.0
Coronene	8.3	3.0	1.9	2.1	2.7	101.5	105.8	69.1
Dibenzo[a,e]pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	3.5	12.9	13.6
Dibenzo[a,i]pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	1.0	16.0	24.1
Dibenzo[a,h]pyrene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	4.3
Thiacoronene	0.3	0.1	0.1	0.06	0.1	1.2	20.1	7.0
Total PAC (ng/m3)	0.17	0.07	0.08	0.08	0.31	1.55	1.60	1.41
R234 Classification (DCM)	P	C	P	P	P	P	C	P

Date Collected	Aug. 15/95	Apr. 12/96	Apr. 14/96	Apr. 10/96	Apr. 16/96	Apr. 20/96	Apr. 23/96	Apr. 26/96
Sampling Site	Gertrude	Pier 25	Pier 25	Pier 25	Pier 25	Pier 25	Pier 25	Pier 25
GC-MS Data File	GERAG15T	25AP12TA	25AP14TA	25AP10TA	25AP16TA	25AP20TA	25AP23TA	25AP26TA
Volume of Air (m3)	1620	1627	1631	1631	1631	1631	1637	1630
Mass Particulate (g)	0.055	0.021	0.014	0.142	0.054	0.058	0.034	0.083
Extracting Solvent:	TOL	TOL	TOL	TOL	TOL	TOL	TOL	TOL
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	<0.09	0.3	<0.09	0.4	1.8	1.1	<0.09	4.5
Phenanthrene	<0.1	23.2	43.3	53.4	32.7	35.6	36.4	112.0
Anthracene	<0.1	1.6	12.4	22.1	1.0	1.6	8.8	1.9
o-Terphenyl	<0.2	0.8	0.8	1.0	0.9	0.8	1.1	1.5
1-Methylphenanthrene	<0.2	2.2	2.9	12.7	8.5	5.4	4.6	14.5
Anthraquinone	<0.5	44.6	52.3	107.5	76.6	48.7	43.6	100.1
Fluoranthene	<0.1	79.8	98.2	265.7	235.0	155.5	143.2	339.5
Pyrene	<0.1	7.2	5.8	138.8	123.5	89.1	80.4	74.6
m-Terphenyl	<0.2	0.7	0.6	2.1	2.1	1.1	1.0	2.8
p-Terphenyl	<0.2	0.6	0.5	1.9	1.6	0.8	0.7	2.2
Benzo[a]fluorene	<0.2	10.8	10.9	42.7	35.4	30.8	25.3	32.3
Benzo[b]fluorene	<0.2	4.3	4.5	21.6	19.3	19.9	14.6	11.1
B21T	<0.1	12.1	8.0	1.4	65.9	31.6	14.8	59.7
Benzo[ghi]fluoranthene	<0.1	27.6	24.5	101.6	72.3	45.6	36.2	83.2
Benzo[c]phenanthrene	<0.2	12.0	10.9	55.1	41.9	26.6	20.6	49.5
B23T	<0.1	1.1	0.6	3.7	2.8	1.8	2.9	1.7
Benz[a]anthracene	<0.1	<0.1	<0.1	104.4	151.7	254.2	209.3	9.4
Cyclopenta[cd]pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Chrysene	<0.1	272.7	246.8	1042.3	951.2	600.1	511.6	901.1
Benzanthrone	0.0	15.6	33.5	162.4	49.3	45.3	35.6	70.7
2-Nitrofluoranthene	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
B[a]A-7,12-dione	<0.5	24.1	38.0	173.4	104.6	45.7	64.7	149.7
Benzo[b]fluoranthene	<0.2	29.9	38.7	520.9	209.5	216.4	181.5	197.9
Benzo[k]fluoranthene	<0.1	4.0	7.4	220.4	93.9	108.5	83.4	59.6
Benzo[j]fluoranthene	<0.1	3.3	4.8	212.4	87.7	100.6	76.0	59.6
Benzo[e]pyrene	<0.1	8.6	5.8	238.1	87.3	98.6	77.5	72.3
Benzo[a]pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	2.3	<0.2	<0.2
Perylene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Indeno[1,2,3-cd]pyrene	<0.2	1.4	0.6	61.3	22.6	24.3	16.8	17.0
Dibenz[a,c]anthracene	<0.2	<0.2	<0.2	<0.2	<0.2	1.9	1.6	5.0
Picene	<0.2	0.9	0.3	11.3	4.3	4.8	3.3	6.3
Benzo[ghi]perylene	<0.2	0.4	0.0	81.9	23.0	23.3	12.8	8.7
Coronene	<0.2	2.4	2.0	59.2	10.8	8.0	5.0	11.4
Dibenzo[a,e]pyrene	<0.2	<0.2	<0.2	2.1	0.7	1.3	0.8	0.3
Dibenzo[a,i]pyrene	<0.2	<0.2	<0.2	3.8	1.4	2.2	1.2	1.7
Dibenzo[a,h]pyrene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	1.2	1.7
Thiacoronene	<0.06	<0.06	<0.06	0.2	0.8	0.4	0.3	0.6
Total PAC (ng/m3)	0.00	0.59	0.65	3.73	2.52	2.03	1.72	2.46
R234 Classification (DCM)	P	P	P	C	C	C	C	C

Date Collected	May 1/96	May 12/96	May 13/96	Sep. 4/97	Sep. 9/97	Sep. 10/97	Sep. 22/97	Sep. 29/97
Sampling Site	Pier 25	Pier 25	Pier 25	Pool	Dofasco 1	Pool	Pool	Pool
GC-MS Data File	25MY01TA	25MY12TA	25MY13TA	POLSE04T	DOFSE09T	POLSE10T	POLSE22T	POLSE29T
Volume of Air (m3)	1632	1632	1639	1684	1634	1797	1382	3035
Mass Particulate (g)	0.054	0.042	0.082	0.085	0.053	0.054	0.062	0.066
Extracting Solvent:	TOL	TOL	TOL	TOL	TOL	TOL	TOL	TOL
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	<0.09	<0.09	<0.09	4.8	1.8	1.5	<0.09	3.4
Phenanthrene	11.0	60.5	92.7	77.5	21.6	17.6	<0.1	38.0
Anthracene	3.1	<0.1	<0.1	0.4	21.6	7.8	<0.1	5.2
o-Terphenyl	1.2	1.1	1.7	0.3	0.3	0.2	<0.2	<0.2
1-Methylphenanthrene	<0.2	8.5	<0.2	7.2	3.4	2.6	8.2	3.9
Anthraquinone	65.5	54.4	91.1	32.6	14.7	10.8	43.1	22.8
Fluoranthene	4.0	136.8	173.3	58.8	33.5	28.3	119.3	43.8
Pyrene	0.6	73.5	31.1	47.3	30.1	25.8	60.7	35.1
m-Terphenyl	1.0	1.1	1.2	0.5	0.4	0.5	1.0	0.4
p-Terphenyl	0.7	0.9	<0.2	0.5	0.3	0.4	1.4	0.3
Benzo[a]fluorene	<0.2	22.8	20.9	5.3	1.7	2.1	8.7	4.3
Benzo[b]fluorene	<0.2	12.4	7.2	3.0	1.0	1.1	4.5	2.7
B21T	<0.1	7.7	15.8	7.4	7.1	5.1	14.6	8.3
Benzo[ghi]fluoranthene	1.7	29.0	34.5	8.5	9.7	14.6	41.4	9.6
Benzo[c]phenanthrene	<0.2	17.0	18.5	2.7	1.5	2.0	8.1	2.7
B23T	<0.1	<0.1	4.3	0.8	0.8	0.6	<0.1	2.6
Benz[a]anthracene	<0.1	176.0	6.4	60.5	19.6	16.4	94.9	53.4
Cyclopenta[cd]pyrene	<0.2	<0.2	<0.2	<0.2	2.5	0.7	<0.2	1.6
Chrysene	62.7	427.3	505.6	73.4	55.3	42.4	214.4	75.1
Benzanthrone	5.2	57.8	310.1	32.0	210.9	8.4	305.7	12.1
2-Nitrofluoranthene	<0.9	<0.9	<0.9	<0.9	0.9	<0.9	28.3	<0.9
B[a]A-7,12-dione	54.3	46.1	270.1	10.2	7.9	3.5	125.3	5.6
Benzo[b]fluoranthene	1.9	258.0	792.9	70.8	38.9	15.4	839.5	46.0
Benzo[k]fluoranthene	<0.1	129.7	299.1	53.6	14.6	8.4	412.0	26.1
Benzo[j]fluoranthene	<0.1	115.5	233.9	44.0	14.4	8.1	406.6	23.0
Benzo[e]pyrene	0.6	112.5	254.2	47.2	27.2	10.6	579.7	33.0
Benzo[a]pyrene	<0.2	<0.2	<0.2	17.6	7.4	1.0	36.3	10.3
Perylene	<0.2	<0.2	<0.2	<0.2	0.8	<0.2	<0.2	2.5
Indeno[1,2,3-cd]pyrene	<0.2	14.8	30.1	63.3	21.9	19.3	498.3	34.8
Dibenz[a,c]anthracene	<0.2	1.3	<0.2	<0.2	<0.2	<0.2	43.2	2.7
Picene	<0.2	2.8	15.1	13.2	2.2	2.7	103.4	6.5
Benzo[ghi]perylene	<0.2	11.9	4.3	55.5	29.8	23.0	602.3	40.3
Coronene	<0.2	5.3	20.6	21.7	13.7	20.1	315.1	17.1
Dibenzo[a,e]pyrene	<0.2	<0.2	<0.2	6.3	1.3	1.7	38.5	3.2
Dibenzo[a,i]pyrene	<0.2	<0.2	<0.2	12.3	1.3	2.9	66.7	4.8
Dibenzo[a,h]pyrene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Thiacoronene	<0.06	<0.06	<0.06	1.6	0.3	0.8	15.2	1.1
Total PAC (ng/m3)	0.21	1.78	3.23	0.84	0.62	0.31	5.02	0.58
R234 Classification (DCM)	C	C	C	C	P	P	C	C

Date Collected	Sep. 4/97	Sep. 9/97	Sep. 10/97	Sep. 22/97	Sep. 29/97	May 8/98	May 9/98	May 10/98
Sampling Site	Dofasco 1	Pool	Dofasco 1	Dofasco 1	Dofasco 1	Dofasco 2	Dofasco 2	Dofasco 2
GC-MS Data File	DOFSE04T	POLSE09T	DOFSE10T	DOFSE22T	DOFSE29T	DOFMY08T	DOFMY09T	DOFMY10T
Volume of Air (m3)	1674	1642	1833	1468	3067	1630	1587	1652
Mass Particulate (g)	0.063	0.039	0.031	0.024	0.101	0.088	0.026	0.009
Extracting Solvent:	TOL	TOL	TOL	TOL	TOL	TOL	TOL	TOL
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	<0.09	0.5	0.2	<0.09	1.8	1.7	<0.09	<0.09
Phenanthrene	0.5	8.7	2.5	35.9	35.0	35.4	<0.1	<0.1
Anthracene	7.8	1.2	0.8	8.8	8.7	4.7	<0.1	<0.1
o-Terphenyl	<0.2	0.2	<0.2	0.4	0.2	0.2	<0.2	<0.2
1-Methylphenanthrene	0.7	1.1	0.8	3.6	3.9	2.6	<0.2	<0.2
Anthraquinone	5.1	5.2	4.6	12.2	12.3	15.3	1.6	34.6
Fluoranthene	14.1	10.9	13.0	39.9	34.8	48.9	6.3	4.8
Pyrene	16.8	9.1	11.6	31.1	25.6	42.8	6.9	0.3
m-Terphenyl	<0.2	<0.2	<0.2	0.5	0.3	0.3	<0.2	<0.2
p-Terphenyl	<0.2	<0.2	<0.2	0.5	0.5	0.3	<0.2	<0.2
Benzo[a]fluorene	2.4	0.4	0.7	2.5	4.0	2.3	0.5	0.4
Benzo[b]fluorene	1.6	0.3	0.4	1.4	2.8	1.4	0.3	<0.2
B21T	5.7	1.4	3.5	5.2	5.6	6.0	1.8	<0.1
Benzo[ghi]fluoranthene	6.8	2.1	5.1	11.9	6.1	10.4	5.9	2.3
Benzo[c]phenanthrene	1.5	0.4	0.7	2.4	2.1	2.5	0.8	<0.2
B23T	0.9	0.2	0.3	0.4	0.6	1.0	<0.1	<0.1
Benz[a]anthracene	24.5	3.4	6.5	19.0	41.2	53.1	7.9	<0.1
Cyclopenta[cd]pyrene	5.4	0.6	0.8	0.7	1.8	0.8	0.5	<0.2
Chrysene	35.7	11.7	24.2	45.9	55.3	67.5	13.6	6.2
Benzanthrone	17.4	21.9	5.1	15.1	19.3	11.9	2.6	6.2
2-Nitrofluoranthene	<0.9	<0.9	<0.9	1.5	<0.9	<0.9	<0.9	<0.9
B[a]A-7,12-dione	3.9	3.8	2.4	4.6	8.6	6.3	1.9	6.0
Benzo[b]fluoranthene	26.7	15.9	8.9	26.3	31.8	49.9	10.7	18.1
Benzo[k]fluoranthene	13.3	3.6	4.0	12.0	20.2	32.6	4.9	3.8
Benzo[j]fluoranthene	11.3	3.3	3.7	14.4	17.8	29.5	4.5	1.8
Benzo[e]pyrene	13.0	11.0	6.0	20.7	23.1	40.4	8.5	5.6
Benzo[a]pyrene	8.1	1.0	1.4	3.5	6.3	20.2	1.2	<0.2
Perylene	0.8	<0.2	<0.2	17.6	<0.2	<0.2	<0.2	2.5
Indeno[1,2,3-cd]pyrene	30.4	5.1	5.6	26.2	32.3	45.8	10.5	4.6
Dibenz[a,c]anthracene	1.8	<0.2	0.0	1.7	3.5	3.7	0.4	<0.2
Picene	3.2	0.4	0.6	3.0	7.3	5.9	0.8	1.5
Benzo[ghi]perylene	45.2	6.5	9.7	34.4	33.6	49.2	18.4	6.9
Coronene	33.9	2.2	6.9	20.9	15.9	22.3	6.9	8.9
Dibenzo[a,e]pyrene	3.5	<0.2	0.4	2.1	3.3	4.8	0.5	<0.2
Dibenzo[a,i]pyrene	4.2	<0.2	0.5	2.4	5.2	8.2	0.5	<0.2
Dibenzo[a,h]pyrene	0.5	<0.4	<0.4	0.5	4.4	<0.4	<0.4	<0.4
Thiacoronene	1.0	0.1	0.2	0.6	0.7	1.8	1.3	0.5
Total PAC (ng/m3)	0.35	0.13	0.13	0.43	0.48	0.63	0.12	0.11
R234 Classification (DCM)	P	P	P	P	C	P	P	P

Date Collected	May 11/98	May 13/98	May 30/98	Jun. 9/98	Jun. 11/98	Jun. 12/98	Jun. 23/98	Jun. 29/98
Sampling Site	Dofasco 2	Dofasco 2	Dofasco 2	Dofasco 2	Dofasco 2	Pool	Dofasco 2	Pool
GC-MS Data File	DOFMY11T	DOFMY13T	DOFMY30T	DOFJN09T	DOFJN11T	POLJN12T	DOFJN23T	POLJN29T
Volume of Air (m3)	1598	1623	1624	1722	1600	1674	1570	1700
Mass Particulate (g)	0.013	0.173	0.050	0.059	0.060	0.048	0.083	0.110
Extracting Solvent:	TOL	TOL	TOL	TOL	TOL	TOL	TOL	TOL
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	1.1
Phenanthrene	<0.1	<0.1	0.1	16.6	25.8	2.9	1.2	22.7
Anthracene	<0.1	19.1	1.0	15.9	26.1	12.8	1.1	18.8
o-Terphenyl	<0.2	<0.2	<0.2	<0.2	0.4	<0.2	<0.2	0.2
1-Methylphenanthrene	<0.2	0.4	<0.2	<0.2	1.6	0.8	6.5	2.6
Anthraquinone	<0.5	26.3	6.4	18.4	14.7	5.6	<0.5	13.6
Fluoranthene	1.8	66.9	2.8	26.0	31.5	15.2	<0.1	41.9
Pyrene	7.2	57.4	0.4	22.1	3.5	15.9	6.7	32.1
m-Terphenyl	<0.2	0.6	<0.2	<0.2	0.4	<0.2	<0.2	0.4
p-Terphenyl	<0.2	0.6	<0.2	0.5	0.4	0.3	<0.2	0.4
Benzo[a]fluorene	0.3	4.5	<0.2	2.0	0.9	1.1	<0.2	3.8
Benzo[b]fluorene	0.3	2.4	<0.2	1.2	0.3	0.7	<0.2	1.8
B21T	1.5	12.6	0.8	3.7	2.1	4.0	4.7	8.1
Benzo[ghi]fluoranthene	8.4	12.9	1.8	9.6	7.3	6.5	11.9	10.1
Benzo[c]phenanthrene	0.8	5.9	0.2	<0.2	1.5	1.1	2.2	2.4
B23T	<0.1	2.4	<0.1	<0.1	<0.1	0.4	<0.1	1.5
Benz[a]anthracene	12.3	45.4	0.5	22.4	43.6	15.5	<0.1	49.5
Cyclopenta[cd]pyrene	<0.2	0.7	<0.2	15.3	11.6	0.6	<0.2	2.3
Chrysene	30.0	83.9	10.7	54.3	43.5	33.2	66.2	76.1
Benzanthrone	3.8	6.1	1.5	7.0	39.6	5.9	32.9	10.3
2-Nitrofluoranthene	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	5.7	<0.9
B[a]A-7,12-dione	2.4	11.6	4.3	6.7	34.9	3.3	33.8	6.6
Benzo[b]fluoranthene	22.9	49.3	8.7	23.2	83.3	14.0	91.1	48.5
Benzo[k]fluoranthene	11.2	32.8	2.0	11.9	26.4	6.8	24.0	24.7
Benzo[j]fluoranthene	9.9	26.4	1.5	11.0	15.7	6.5	14.7	23.8
Benzo[e]pyrene	16.5	32.6	3.4	15.9	35.2	10.0	46.2	36.0
Benzo[a]pyrene	4.3	0.7	0.4	15.9	35.1	5.0	<0.2	16.1
Perylene	0.9	0.8	0.0	<0.2	32.9	0.3	<0.2	0.5
Indeno[1,2,3-cd]pyrene	15.7	44.3	2.6	18.0	16.6	10.9	23.7	27.2
Dibenz[a,c]anthracene	1.0	<0.2	1.0	1.4	11.7	0.4	<0.2	1.9
Picene	1.8	9.7	0.7	3.2	10.9	1.5	10.2	4.1
Benzo[ghi]perylene	16.1	40.4	2.1	21.0	2.4	13.6	7.7	31.1
Coronene	6.5	16.2	6.9	13.0	40.2	7.9	57.9	12.0
Dibenzo[a,e]pyrene	1.2	2.0	0.3	1.6	1.0	1.2	1.5	2.4
Dibenzo[a,i]pyrene	2.1	3.7	0.5	3.0	3.8	0.2	3.9	<0.2
Dibenzo[a,h]pyrene	<0.4	<0.4	<0.4	<0.4	3.8	<0.4	<0.4	<0.4
Thiacoronene	0.6	1.2	0.5	1.0	1.5	0.4	1.6	0.7
Total PAC (ng/m3)	0.18	0.62	0.06	0.36	0.61	0.20	0.45	0.53
R234 Classification (DCM)	P	C	P	P	P	P	P	P

Date Collected	July 6/98	May 8/98	May 9/98	May 10/98	May 11/98	May 13/98	May 30/98	Jun. 9/98
Sampling Site	Dofasco 2	Pool	Pool	Pool	Pool	Pool	Pool	Pool
GC-MS Data File	DOFJL06T	POLMY08T	POLMY09T	POLMY10T	POLMY11T	POLMY13T	POLMY30T	POLJN09T
Volume of Air (m3)	1638	1629	1588	1661	1536	1626	1632	1438
Mass Particulate (g)	0.043	0.036	0.014	0.007	0.006	0.044	0.036	0.020
Extracting Solvent:	TOL	TOL	TOL	TOL	TOL	TOL	TOL	TOL
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)
Dibenzothiophene	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Phenanthrene	<0.1	<0.1	<0.1	3.6	<0.1	<0.1	0.3	<0.1
Anthracene	<0.1	<0.1	<0.1	0.7	<0.1	<0.1	0.2	<0.1
o-Terphenyl	0.2	<0.2	<0.2	0.3	<0.2	<0.2	<0.2	<0.2
1-Methylphenanthrene	1.0	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Anthraquinone	10.3	<0.5	<0.5	1.5	<0.5	1.5	0.6	<0.5
Fluoranthene	28.4	0.3	<0.1	1.0	0.2	3.6	2.3	0.8
Pyrene	2.8	0.7	<0.1	<0.1	0.7	5.9	4.0	2.2
m-Terphenyl	0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
p-Terphenyl	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Benzo[a]fluorene	0.6	<0.2	<0.2	<0.2	0.4	1.0	<0.2	<0.2
Benzo[b]fluorene	<0.2	<0.2	<0.2	<0.2	<0.2	0.6	<0.2	<0.2
B21T	2.0	<0.1	<0.1	<0.1	0.3	2.6	0.5	0.8
Benzo[ghi]fluoranthene	6.6	1.1	0.2	0.3	1.4	6.4	2.0	2.2
Benzo[c]phenanthrene	1.3	<0.2	<0.2	<0.2	<0.2	0.9	<0.2	0.3
B23T	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	<0.1	0.2
Benz[a]anthracene	<0.1	2.4	0.3	0.2	2.2	18.8	4.1	4.6
Cyclopenta[cd]pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	1.7	<0.2	0.4
Chrysene	39.4	5.5	0.9	1.0	4.7	24.6	7.8	10.0
Benzanthrone	543.7	1.2	0.2	0.3	0.7	3.4	1.3	1.6
2-Nitrofluoranthene	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
B[a]A-7,12-dione	350.9	0.8	<0.5	<0.5	<0.5	2.0	0.7	1.3
Benzo[b]fluoranthene	1177.9	3.4	1.3	1.2	6.0	10.6	6.7	9.6
Benzo[k]fluoranthene	378.9	1.2	0.3	0.3	3.0	5.9	3.8	5.0
Benzo[j]fluoranthene	165.6	1.3	0.2	0.1	2.6	5.5	3.5	4.6
Benzo[e]pyrene	448.2	2.2	0.9	0.2	4.5	7.8	5.6	7.3
Benzo[a]pyrene	<0.2	<0.2	<0.2	<0.2	2.0	2.9	2.7	3.5
Perylene	<0.2	<0.2	<0.2	<0.2	0.4	0.4	0.7	0.6
Indeno[1,2,3-cd]pyrene	140.7	2.7	0.8	<0.2	3.8	12.2	5.7	8.2
Dibenz[a,c]anthracene	<0.2	<0.2	<0.2	<0.2	1.0	<0.2	0.4	1.6
Picene	104.0	0.3	<0.2	<0.2	0.3	1.7	0.5	0.8
Benzo[ghi]perylene	16.2	2.4	0.9	<0.2	4.4	16.6	7.2	9.0
Coronene	676.7	1.9	0.4	0.3	2.1	10.2	3.8	3.7
Dibenzo[a,e]pyrene	<0.2	<0.2	<0.2	<0.2	0.3	1.3	<0.2	0.6
Dibenzo[a,i]pyrene	<0.2	<0.2	<0.2	<0.2	0.5	<0.2	<0.2	0.8
Dibenzo[a,h]pyrene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Thiacoronene	16.8	0.1	<0.06	<0.06	0.2	0.4	0.4	0.3
Total PAC (ng/m3)	4.10	0.03	0.01	0.01	0.04	0.15	0.06	0.08
R234 Classification (DCM)	P	P	P	P	P	P	P	P

Date Collected	Jun. 11/98	Jun. 12/98	Jun. 23/98	Jun. 29/98	July 6/98	
Sampling Site	Pool	Dofasco 2	Pool	Dofasco 2	Pool	
GC-MS Data File	POLJN11T	DOFJN12T	POLJN23T	DOFJN29T	POLJL06T	
Volume of Air (m3)	1606	1670	1569	1680	1639	DETECTION
Mass Particulate (g)	0.028	0.070	0.062	0.109	0.017	LIMIT
Extracting Solvent:	TOL	TOL	TOL	TOL	TOL	(PG/M3)
	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	(pg/m3)	
Dibenzothiophene	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Phenanthrene	<0.1	<0.1	3.4	<0.1	5.7	<0.1
Anthracene	<0.1	<0.1	4.1	<0.1	1.7	<0.1
o-Terphenyl	<0.2	<0.2	<0.2	<0.2	0.2	<0.2
1-Methylphenanthrene	<0.2	<0.2	2.7	<0.2	<0.2	<0.2
Anthraquinone	0.9	20.5	17.3	<0.5	2.5	<0.5
Fluoranthene	3.7	35.1	29.6	<0.1	4.0	<0.1
Pyrene	4.2	0.8	23.9	0.8	0.9	<0.1
m-Terphenyl	<0.2	<0.2	0.6	<0.2	<0.2	<0.2
p-Terphenyl	<0.2	<0.2	0.3	<0.2	<0.2	<0.2
Benzo[a]fluorene	0.4	<0.2	3.3	<0.2	<0.2	<0.2
Benzo[b]fluorene	0.3	<0.2	2.3	<0.2	<0.2	<0.2
B21T	0.8	3.6	3.6	<0.1	<0.1	<0.1
Benzo[ghi]fluoranthene	2.4	6.9	12.2	8.9	0.8	<0.1
Benzo[c]phenanthrene	0.5	1.2	1.6	2.4	<0.2	<0.2
B23T	<0.1	<0.1	0.5	<0.1	<0.1	<0.1
Benz[a]anthracene	4.7	<0.1	6.8	<0.1	<0.1	<0.1
Cyclopenta[cd]pyrene	0.4	<0.2	<0.2	<0.2	<0.2	<0.2
Chrysene	12.5	50.1	47.8	77.9	4.3	<0.1
Benzanthrone	2.2	39.2	24.4	82.7	1.2	<0.3
2-Nitrofluoranthene	<0.9	<0.9	6.6	<0.9	<0.9	<0.9
B[a]A-7,12-dione	1.3	56.2	18.5	101.0	1.4	<0.5
Benzo[b]fluoranthene	4.9	95.2	54.1	230.1	3.6	<0.2
Benzo[k]fluoranthene	2.3	21.7	19.2	58.0	0.6	<0.1
Benzo[j]fluoranthene	2.3	4.7	20.4	11.5	0.6	<0.1
Benzo[e]pyrene	3.4	11.2	39.3	46.8	1.6	<0.1
Benzo[a]pyrene	1.7	<0.2	<0.2	<0.2	<0.2	<0.2
Perylene	<0.2	<0.2	<0.2	2.6	<0.2	<0.2
Indeno[1,2,3-cd]pyrene	3.5	1.3	28.8	5.0	0.6	<0.2
Dibenz[a,c]anthracene	0.8	<0.2	0.9	<0.2	0.5	<0.2
Picene	0.4	9.1	6.5	22.3	<0.2	<0.2
Benzo[ghi]perylene	4.5	<0.2	33.2	5.9	<0.2	<0.2
Coronene	2.5	42.4	36.9	59.3	1.4	<0.2
Dibenzo[a,e]pyrene	0.3	<0.2	1.7	2.0	<0.2	<0.2
Dibenzo[a,i]pyrene	0.5	2.8	3.0	7.9	<0.2	<0.2
Dibenzo[a,h]pyrene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Thiacoronene	0.1	<0.06	0.8	<0.06	<0.06	<0.06
Total PAC (ng/m3)	0.06	0.40	0.45	0.73	0.03	
R234 Classification (DCM)	P	P	P	P	P	

Appendix VII: Concentrations of TPAC and thiacoronene in sequential extracts of ambient air samples (ng/m^3 and pg/m^3)

Appendix VII: Relative amounts of thiacoronene (pg/m^3) and total concentration of PAC (ng/m^3) in air particulate extracts

SAMPLE SET	SAMPLE NAME (site - date)	Thiacoronene in DCM (pg/m^3)	Thiacoronene in Toluene (pg/m^3)	TPAC in DCM (ng/m^3)	TPAC in Toluene (ng/m^3)
1996 - Downwind of the Coke Ovens	pier 25 - 04/10/96	439	0.18	242	3.73
	pier 25 - 04/16/96	130	0.80	62.1	2.52
	pier 25 - 04/20/96	107	0.39	133	2.04
	pier 25 - 04/23/96	76.7	0.26	68.6	1.72
	pier 25 - 04/26/96	152	0.64	138	2.47
	pier 25 - 05/01/96	49.6	nd	44.7	0.22
	pier 25 - 05/12/96	47.7	nd	30.2	1.79
	pier 25 - 05/13/96	73.1	nd	122	3.25
Average		**134**	**0**	**105**	**2**
standard deviation		**130**	**0**	**69**	**1**
RSD		**97**	**57**	**66**	**48**
1995- Downwind of the Columbian Carbon Black Plant	philip - 07/14/95	31.4	4.84	7.28	0.49
	philip - 07/17/95	66.8	1.12	13.4	0.29
	philip - 07/18/95	123	6.59	31.2	0.82
	philip - 07/19/95	186	8.09	19.5	0.75
	philip - 07/20/95	156	3.64	12.1	2.28
	philip - 07/23/95	75.2	21.5	19.2	1.16
	philip - 07/29/95	141	13.2	46.5	1.33
	philip - 08/02/95	108	1.2	5.9	1.60
	philip - 08/15/95	68	7.0	23.6	1.40
Average		**106**	**7**	**20**	**1**
standard deviation		**50**	**6**	**13**	**1**
RSD		**47**	**86**	**64**	**55**
1997- Downwind of the Columbian Carbon Black Plant	pool - 09/04/97	30.1	1.63	16.1	0.84
	dof.1 - 09/09/97	2.9	0.32	2.57	0.62
	pool - 09/10/97	5.6	0.80	2.80	0.31
	pool - 09/22/97	13.6	15.2	6.89	5.04
	pool - 09/29/97	18.1	1.10	8.84	0.59
Average		**14**	**3.8**	**7.4**	**1.5**
standard deviation		**11**	**6.4**	**5.5**	**2.0**
RSD		**77**	**170**	**74**	**140**
1998- Downwind of the Columbian Carbon Black Plant	Dof.2 - 05/08/98	10.1	1.83	8.92	0.64
	Dof.2 - 05/09/98	6.0	1.29	1.72	0.12
	Dof.2 - 05/10/98	1.3	0.52	0.94	0.13
	Dof.2 - 05/11/98	2.1	0.56	2.48	0.18
	Dof.2 - 05/13/98	58.0	1.21	76.7	0.62
	Dof.2 - 05/30/98	6.5	0.46	2.99	0.06
	Dof.2 - 06/09/98	6.9	1.00	4.59	0.36
	Dof.2 - 06/11/98	2.0	1.50	1.61	0.63
	pool - 06/12/98	4.8	0.41	2.23	0.21
	Dof.2 - 06/23/98	6.1	1.55	3.56	0.46
	pool - 06/29/98	7.9	0.70	4.76	0.54
	Dof.2 - 07/06/98	3.7	16.8	1.61	4.11
Average		**10**	**2**	**9**	**1**
standard deviation		**15**	**5**	**21**	**1**
RSD		**160**	**200**	**230**	**170**

*n/a (not reported)

Appendix VII: (continued)

SAMPLE SET	SAMPLE NAME (site - date)	Thiacoronene in DCM (pg/m^3)	Thiacoronene in Toluene (pg/m^3)	TPAC in DCM (ng/m^3)	TPAC in Toluene (ng/m^3)
1996 - Upwind of the Coke Ovens	Pier 25 - 04/12/96	0.6	<0.06	2.82	0.59
	Pier 25 - 04/14/96	1.5	<0.06	15.2	0.66
Average		**1**		**9**	**1**
standard deviation					
RSD					
1995- Upwind of the Columbian Carbon Black Plant	Gert. - 07/17/95	2.7	0.10	1.30	0.24
	Gert. - 07/18/95	2.8	0.26	1.39	0.18
	Gert. - 07/19/95	3.8	0.08	2.48	0.07
	Gert. - 07/20/95	n/a	0.10	0.7	0.09
	Gert. - 07/23/95	n/a	0.06	0.5	0.09
	Gert. - 07/29/95	n/a	0.12	1.1	0.32
	Gert. - 08/02/95	32.7	20.1	29.8	1.6
	Gert. - 08/15/95	n/a	<0.06	2.6	0
Average		**11**	**5.1**	**8.7**	**0.5**
standard deviation		15	10	14	0.7
RSD		140	190	160	140
1997- Upwind of the Columbian Carbon Black Plant	Dof.1 - 09/04/97	9.4	0.98	5.34	0.35
	pool - 09/09/97	0.7	0.06	0.84	0.14
	Dof.1 - 09/10/97	1.7	0.17	1.08	0.14
	Dof.1 - 09/22/97	4.2	0.65	3.02	0.44
	Dof.1 - 09/29/97	21.9	0.71	15.6	0.49
Average		**7.6**	**0.5**	**5.2**	**0.3**
standard deviation		8.7	0.4	6.1	0.2
RSD		120	80	120	54
1998- Upwind of the Columbian Carbon Black Plant	pool - 05/08/98	0.7	0.10	0.87	0.03
	pool - 05/09/98	0.3	<0.06	0.35	0.01
	pool - 05/10/98	0.2	<0.06	0.20	0.02
	pool - 05/11/98	0.2	0.22	0.37	0.04
	pool - 05/13/98	7.1	0.40	4.29	0.15
	pool - 05/30/98	1.7	0.37	1.10	0.07
	pool - 06/09/98	2.0	0.34	1.32	0.08
	pool - 06/11/98	0.5	0.10	0.70	0.06
	Dof.2 - 06/12/98	7.4	<0.06	3.29	0.41
	pool - 06/23/98	3.1	0.80	2.73	0.46
	Dof.2 - 06/29/98	10.2	<0.06	5.69	0.73
	pool - 07/06/98	0.5	0.04	0.48	0.04
Average		**2.8**	**0.3**	**1.8**	**0.2**
standard deviation		3.5	0.2	1.8	0.2
RSD		120	83	100	130

*n/a (not reported)

Appendix VIII: Concentrations of metals in ambient air samples (mass/m^3) including normalized data and Mn-Sn Metal Index values

Appendix VIII: Metal data for ambient air samples including (i) metal concentrations (mass/m3), (ii) normalized metal values, (iii) Mn-Sn Index, (iv) TPAC (ng/m3), (v) R234

Date [Site]	Filter #	V (ng/m3)	Cr (ng/m3)	Mn (ng/m3)	Fe (ug/m3)	Ni (ng/m3)	Cu (ng/m3)	Zn (ug/m3)
14/4/96 [P25]	1491	5.29	6.31	12.75	0.28	3.45	21.87	0.13
13/4/96 [P25]	1492	7.02	7.82	20.21	0.35	4.13	19.33	0.16
12/4/96 [P25]	1493	6.01	6.55	16.81	0.28	5.00	26.24	0.18
9/4/96 [P25]	1494	20.34	17.27	114.29	1.26	10.40	37.08	0.24
5/4/96 [P25]	1495	6.52	10.05	27.03	0.85	6.53	54.10	0.18
6/4/96 [P25]	1496	3.44	7.52	43.16	1.15	5.81	82.98	0.24
11/4/96 [P25]	1497	8.91	12.06	165.96	1.61	6.36	44.38	0.62
10/4/96 [P25]	1498	22.89	12.60	299.70	4.05	11.78	43.16	0.60
8/4/96 [P25]	1499	9.99	10.95	87.23	1.44	8.71	64.13	0.26
7/4/96 [P25]	1500	16.46	10.42	131.31	1.23	10.84	57.45	0.24
/4/96 [P25]	1471	9.56	10.44	104.26	1.22	6.56	30.03	0.28
/4/96 [P25]	1472	16.37	12.63	177.51	1.63	8.88	24.33	0.26
/4/96 [P25]	1473	14.12	10.86	483.28	3.11	9.42	53.19	0.49
25/4/96 [P25]	1378	7.26	5.82	145.59	1.22	5.75	23.50	0.21
24/4/96 [P25]	1379	7.57	5.49	40.43	0.61	3.97	37.69	0.18
24/4/96 [P25]	1379 replicate	7.27	6.14	37.08	0.55	3.96	36.17	0.18
23/4/96 [P25]	1380	9.43	8.16	61.40	0.74	5.30	23.24	0.30
22/4/96 [P25]	1381	7.30	7.46	33.13	0.43	3.20	17.17	0.15
1/5/96 [P25]	1411	6.47	7.94	158.36	1.27	5.49	25.45	0.35
30/4/96 [P25]	1412	5.60	6.83	132.52	1.05	4.85	22.06	0.17
29/4/96 [P25]	1413	5.40	6.41	108.21	0.83	4.18	19.72	0.24
28/4/96 [P25]	1414	6.65	7.25	37.39	0.50	2.93	14.54	0.13
26/4/96 [P25]	1416	13.01	10.32	234.04	1.94	5.39	21.27	0.35
13/5/96 [P25]	1479	8.10	12.47	215.81	2.02	6.52	28.82	0.65
12/5/96 [P25]	1480	8.83	10.24	116.41	1.02	4.51	17.43	0.29
11/5/96 [P25]	1481	6.18	6.89	18.55	0.34	3.80	16.26	0.12
10/5/96 [P25]	1482	6.79	7.12	31.61	0.46	4.22	16.22	0.19
8/5/96 [P25]	1484	7.13	4.91	44.38	0.35	3.75	20.84	0.12
20/4/96 [P25]	1485	5.64	6.98	89.36	0.95	3.98	20.45	0.49
/4/96 [P25]	1486	7.24	7.26	133.74	1.08	7.30	34.95	0.25
18/4/96 [P25]	1487	8.95	6.80	74.77	0.80	4.59	34.04	0.18
17/4/96 [P25]	1488	11.93	9.81	275.08	1.72	6.39	33.43	0.32
16/4/96 [P25]	1489	13.66	14.30	184.80	1.86	7.33	25.63	0.21
15/4/96 [P25]	1490	15.81	15.67	50.46	1.04	9.70	27.40	0.44
5/5/96 [P25]	1503	5.15	4.75	23.19	0.26	2.73	15.78	0.11
4/9/97 [DO1]	1446	5.35	4.84	213.52	1.54	2.86	26.30	0.17
9/9/97 [POL]	1437	4.10	0.00	7.95	0.20	2.98	15.55	0.12
10/9/97 [DO1]	1436	2.86	3.41	24.29	0.47	1.94	16.10	0.10
22/9/97 [DO1]	5002	21.59	13.20	36.08	0.77	7.04	21.40	0.44
29/9/97 [DO1]	5009	12.29	8.86	167.87	1.38	4.95	18.89	0.49
4/9/97 [POL]	1445	5.85	5.50	287.80	1.53	3.97	54.97	0.38
9/9/97 [DO1]	1438	4.71	10.13	59.99	0.88	3.81	48.47	0.19
10/9/97 [POL]	1435	2.39	3.61	51.24	0.55	2.38	33.06	0.23
22/9/97 [POL]	5000	23.44	15.76	237.49	1.50	8.18	62.33	0.55

Date [Site]	Filter #	V (ng/m3)	Cr (ng/m3)	Mn (ng/m3)	Fe (ug/m3)	Ni (ng/m3)	Cu (ng/m3)	Zn (ug/m3)
29/9/97 [POL]	5010	11.70	8.13	97.70	0.93	3.82	25.94	0.47
8/5/98 [POL]	5029	26.68	16.47	15.49	0.67	10.27	17.18	0.18
9/5/98 [POL]	5033	24.63	14.74	11.41	0.53	8.10	10.41	0.19
10/5/98 [POL]	5035	17.20	8.82	12.27	0.34	4.64	21.81	0.18
11/5/98 [POL]	5037	36.42	22.65	15.14	0.82	12.87	15.30	0.35
13/5/98 [POL]	5040	39.28	25.39	58.46	1.31	13.95	24.12	0.38
30/5/98 [POL]	6003	43.07	27.02	48.53	1.16	15.77	22.29	0.66
9/6/98 [POL]	6020	46.48	29.77	46.48	1.31	16.91	19.56	0.46
11/6/98 [POL]	6022	36.99	23.28	18.63	0.95	15.18	14.29	0.30
23/6/98 [POL]	6041	40.39	26.32	47.01	1.27	15.81	23.94	0.38
29/6/98 [DO2]	6050	29.76	23.27	170.91	2.05	12.22	37.42	0.45
6/7/98 [POL]	6057	34.13	24.47	19.92	0.90	14.82	15.35	0.30
12/6/98 [DO2]	6024	37.35	26.75	130.44	1.71	15.31	29.02	0.57
8/5/98 [DO2]	5030	31.59	20.50	105.08	1.36	13.10	41.30	0.41
9/5/98 [DO2]	5032	22.18	13.54	22.84	0.60	8.31	20.07	0.20
10/5/98 [DO2]	5034	24.65	13.08	11.87	0.50	8.15	16.43	0.40
11/5/98 [DO2]	5036	35.94	24.74	37.18	1.03	14.15	30.90	0.56
13/5/98 [DO2]	5041	42.40	32.94	261.40	2.94	18.47	67.71	0.58
30/5/98 [DO2]	6004	46.33	25.99	76.51	1.35	15.19	84.74	0.45
9/6/98 [DO2]	6019	40.25	26.39	155.53	2.05	18.54	45.42	0.51
11/6/98 [DO2]	6021	47.03	28.37	90.66	1.47	17.68	32.49	0.42
29/6/98 [POL]	6049	32.32	25.41	101.63	1.79	14.67	52.42	0.69
23/6/98 [DO2]	6042	49.82	33.73	123.29	2.22	21.44	63.69	0.90
12/6/98 [POL]	6023	37.26	27.12	75.71	1.37	16.03	53.82	0.35
6/7/98 [DO2]	6058	35.97	25.60	57.42	1.31	15.34	25.68	0.42
Normalization Factor		7.29	10.18	44.53	0.46	6.69	54.71	0.20

* site abbreviations: P25 (pier 25), DO1 (dofasco 1), DO2 (dofasco 2), POL (pool); for site location refer to map 2.1

Date [Site]	Filter #	As (ng/m3)	Sn (ng/m3)	Pb (ng/m3)	Ti (ug/m3)	V Normalized	Cr Normalized	Mn Normalized
14/4/96 [P25]	1491	1.66	0.97	6.90	0.18	0.13	0.24	0.27
13/4/96 [P25]	1492	2.33	1.48	8.66	0.23	0.17	0.30	0.43
12/4/96 [P25]	1493	1.99	1.04	8.70	0.21	0.15	0.25	0.36
9/4/96 [P25]	1494	4.15	2.01	33.74	0.19	0.50	0.66	2.43
5/4/96 [P25]	1495	3.25	3.36	23.67	0.23	0.16	0.38	0.57
6/4/96 [P25]	1496	2.11	2.84	36.78	0.08	0.09	0.29	0.92
11/4/96 [P25]	1497	3.72	12.09	53.19	0.19	0.22	0.46	3.53
10/4/96 [P25]	1498	7.81	6.53	134.65	0.13	0.57	0.48	6.37
8/4/96 [P25]	1499	3.24	4.36	42.55	0.19	0.25	0.42	1.86
7/4/96 [P25]	1500	5.20	4.44	55.93	0.20	0.41	0.40	2.79
/4/96 [P25]	1471	3.31	9.47	31.31	0.24	0.24	0.40	2.22
/4/96 [P25]	1472	4.65	5.29	62.01	0.34	0.41	0.48	3.78
/4/96 [P25]	1473	4.63	35.87	57.14	0.09	0.35	0.41	10.28
25/4/96 [P25]	1378	2.06	2.15	46.20	0.11	0.18	0.22	3.10
24/4/96 [P25]	1379	2.08	0.00	15.99	0.14	0.19	0.21	0.86
24/4/96 [P25]	1379 replicate	2.00	0.00	15.62	0.13	0.18	0.23	0.79
23/4/96 [P25]	1380	3.11	2.35	89.06	0.18	0.23	0.31	1.31
22/4/96 [P25]	1381	2.74	0.00	16.26	0.19	0.18	0.28	0.70
1/5/96 [P25]	1411	3.25	10.35	51.06	0.14	0.16	0.30	3.37
30/4/96 [P25]	1412	1.98	2.82	17.81	0.14	0.14	0.26	2.82
29/4/96 [P25]	1413	3.02	7.08	33.13	0.14	0.13	0.24	2.30
28/4/96 [P25]	1414	2.55	0.00	11.45	0.22	0.16	0.28	0.80
26/4/96 [P25]	1416	4.38	3.17	71.12	0.19	0.32	0.39	4.98
13/5/96 [P25]	1479	4.33	26.64	63.53	0.19	0.20	0.47	4.59
12/5/96 [P25]	1480	2.90	0.00	22.74	0.23	0.22	0.39	2.48
11/5/96 [P25]	1481	3.62	1.51	10.33	0.21	0.15	0.26	0.39
10/5/96 [P25]	1482	2.09	0.00	7.95	0.22	0.17	0.27	0.67
8/5/96 [P25]	1484	1.51	1.00	12.60	0.14	0.18	0.19	0.94
20/4/96 [P25]	1485	2.63	7.39	47.42	0.17	0.14	0.27	1.90
/4/96 [P25]	1486	2.40	2.46	25.85	0.15	0.18	0.28	2.84
18/4/96 [P25]	1487	2.35	0.80	18.86	0.16	0.22	0.26	1.59
17/4/96 [P25]	1488	3.62	5.74	44.68	0.19	0.30	0.37	5.85
16/4/96 [P25]	1489	5.52	1.26	52.58	0.31	0.34	0.54	3.93
15/4/96 [P25]	1490	4.81	3.20	41.03	0.44	0.39	0.60	1.07
5/5/96 [P25]	1503	1.84	0.00	7.62	0.13	0.13	0.18	0.49
4/9/97 [DO1]	1446	1.26	2.73	15.52	0.03	0.13	0.18	4.54
9/9/97 [POL]	1437	1.43	1.72	9.77	0.06	0.10	0.00	0.17
10/9/97 [DO1]	1436	1.14	0.90	5.35	0.09	0.07	0.13	0.52
22/9/97 [DO1]	5002	1.96	0.94	13.43	0.47	0.53	0.50	0.77
29/9/97 [DO1]	5009	2.08	3.91	38.58	0.22	0.30	0.34	3.57
4/9/97 [POL]	1445	2.38	3.23	29.69	0.05	0.14	0.21	6.12
9/9/97 [DO1]	1438	6.09	1.92	61.20	0.06	0.12	0.38	1.28
10/9/97 [POL]	1435	0.92	1.35	11.60	0.06	0.06	0.14	1.09
22/9/97 [POL]	5000	2.91	2.99	54.45	0.50	0.58	0.60	5.05
29/9/97 [POL]	5010	1.36	1.56	20.88	0.24	0.29	0.31	2.08
8/5/98 [POL]	5029	1.95	0.00	9.19	0.66	0.66	0.63	0.33

Date [Site]	Filter #	As (ng/m3)	Sn (ng/m3)	Pb (ng/m3)	Ti (ug/m3)	V Normalized	Cr Normalized	Mn Normalized
9/5/98 [POL]	5033	1.46	0.00	6.80	0.58	0.61	0.56	0.24
10/5/98 [POL]	5035	1.37	1.49	5.78	0.34	0.43	0.34	0.26
11/5/98 [POL]	5037	2.01	1.49	7.26	1.01	0.90	0.86	0.32
13/5/98 [POL]	5040	2.51	0.00	16.97	1.06	0.97	0.96	1.24
30/5/98 [POL]	6003	3.04	2.12	17.33	1.22	1.07	1.03	1.03
9/6/98 [POL]	6020	3.08	2.67	15.84	1.39	1.15	1.13	0.99
11/6/98 [POL]	6022	2.52	0.00	10.59	1.11	0.92	0.88	0.40
23/6/98 [POL]	6041	3.65	4.41	20.05	1.19	1.00	1.00	1.00
29/6/98 [DO2]	6050	2.69	1.74	28.00	0.79	0.74	0.88	3.64
6/7/98 [POL]	6057	2.72	1.81	11.21	1.11	0.85	0.93	0.42
12/6/98 [DO2]	6024	2.73	1.60	21.96	1.08	0.92	1.02	2.77
8/5/98 [DO2]	5030	2.78	5.39	30.13	0.69	0.78	0.78	2.24
9/5/98 [DO2]	5032	1.47	1.26	14.99	0.50	0.55	0.51	0.49
10/5/98 [DO2]	5034	1.29	0.00	12.40	0.53	0.61	0.50	0.25
11/5/98 [DO2]	5036	2.15	0.00	15.34	1.01	0.89	0.94	0.79
13/5/98 [DO2]	5041	3.25	6.38	68.32	0.77	1.05	1.25	5.56
30/5/98 [DO2]	6004	3.35	30.22	32.92	0.96	1.15	0.99	1.63
9/6/98 [DO2]	6019	3.21	4.27	127.07	1.04	1.00	1.00	3.31
11/6/98 [DO2]	6021	3.21	2.77	93.13	1.23	1.16	1.08	1.93
29/6/98 [POL]	6049	2.86	2.60	57.66	0.89	0.80	0.97	2.16
23/6/98 [DO2]	6042	4.96	9.36	70.00	1.41	1.23	1.28	2.62
12/6/98 [POL]	6023	2.79	2.45	17.82	1.06	0.92	1.03	1.61
6/7/98 [DO2]	6058	3.20	2.05	106.08	1.12	0.89	0.97	1.22
Normalization Factor		3.80	2.43	24.32	0.23			

Date [Site]	Filter #	Fe Normalized	Ni Normalized	Cu Normalized	Zn Normalized	As Normalized	Sn Normalized	Pb Normalized
14/4/96 [P25]	1491	0.22	0.22	0.91	0.34	0.45	0.22	0.34
13/4/96 [P25]	1492	0.28	0.26	0.81	0.43	0.64	0.34	0.43
12/4/96 [P25]	1493	0.22	0.32	1.10	0.46	0.55	0.24	0.43
9/4/96 [P25]	1494	1.00	0.66	1.55	0.63	1.14	0.46	1.68
5/4/96 [P25]	1495	0.67	0.41	2.26	0.49	0.89	0.76	1.18
6/4/96 [P25]	1496	0.91	0.37	3.47	0.65	0.58	0.65	1.83
11/4/96 [P25]	1497	1.27	0.40	1.85	1.65	1.02	2.74	2.65
10/4/96 [P25]	1498	3.20	0.75	1.80	1.59	2.14	1.48	6.72
8/4/96 [P25]	1499	1.14	0.55	2.68	0.69	0.89	0.99	2.12
7/4/96 [P25]	1500	0.97	0.69	2.40	0.64	1.43	1.01	2.79
/4/96 [P25]	1471	0.97	0.41	1.25	0.76	0.91	2.15	1.56
/4/96 [P25]	1472	1.29	0.56	1.02	0.70	1.27	1.20	3.09
/4/96 [P25]	1473	2.46	0.60	2.22	1.30	1.27	8.14	2.85
25/4/96 [P25]	1378	0.96	0.36	0.98	0.57	0.57	0.49	2.30
24/4/96 [P25]	1379	0.48	0.25	1.57	0.48	0.57	0.00	0.80
24/4/96 [P25]	1379 replicate	0.43	0.25	1.51	0.48	0.55	0.00	0.78
23/4/96 [P25]	1380	0.59	0.33	0.97	0.79	0.85	0.53	4.44
22/4/96 [P25]	1381	0.34	0.20	0.72	0.39	0.75	0.00	0.81
1/5/96 [P25]	1411	1.00	0.35	1.06	0.93	0.89	2.35	2.55
30/4/96 [P25]	1412	0.83	0.31	0.92	0.44	0.54	0.64	0.89
29/4/96 [P25]	1413	0.66	0.26	0.82	0.63	0.83	1.61	1.65
28/4/96 [P25]	1414	0.39	0.19	0.61	0.35	0.70	0.00	0.57
26/4/96 [P25]	1416	1.53	0.34	0.89	0.93	1.20	0.72	3.55
13/5/96 [P25]	1479	1.60	0.41	1.20	1.73	1.19	6.05	3.17
12/5/96 [P25]	1480	0.81	0.29	0.73	0.78	0.79	0.00	1.13
11/5/96 [P25]	1481	0.27	0.24	0.68	0.32	0.99	0.34	0.52
10/5/96 [P25]	1482	0.37	0.27	0.68	0.50	0.57	0.00	0.40
8/5/96 [P25]	1484	0.27	0.24	0.87	0.33	0.41	0.23	0.63
20/4/96 [P25]	1485	0.75	0.25	0.85	1.30	0.72	1.68	2.37
/4/96 [P25]	1486	0.85	0.46	1.46	0.66	0.66	0.56	1.29
18/4/96 [P25]	1487	0.63	0.29	1.42	0.49	0.64	0.18	0.94
17/4/96 [P25]	1488	1.36	0.40	1.40	0.84	0.99	1.30	2.23
16/4/96 [P25]	1489	1.47	0.46	1.07	0.57	1.51	0.29	2.62
15/4/96 [P25]	1490	0.82	0.61	1.14	1.17	1.32	0.73	2.05
5/5/96 [P25]	1503	0.21	0.17	0.66	0.29	0.50	0.00	0.38
4/9/97 [DO1]	1446	1.22	0.18	1.10	0.45	0.35	0.62	0.77
9/9/97 [POL]	1437	0.16	0.19	0.65	0.33	0.39	0.39	0.49
10/9/97 [DO1]	1436	0.37	0.12	0.67	0.26	0.31	0.20	0.27
22/9/97 [DO1]	5002	0.61	0.45	0.89	1.18	0.54	0.21	0.67
29/9/97 [DO1]	5009	1.09	0.31	0.79	1.29	0.57	0.89	1.92
4/9/97 [POL]	1445	1.21	0.25	2.30	1.02	0.65	0.73	1.48
9/9/97 [DO1]	1438	0.70	0.24	2.02	0.50	1.67	0.44	3.05
10/9/97 [POL]	1435	0.44	0.15	1.38	0.62	0.25	0.31	0.58
22/9/97 [POL]	5000	1.18	0.52	2.60	1.46	0.80	0.68	2.72
29/9/97 [POL]	5010	0.74	0.24	1.08	1.24	0.37	0.35	1.04
8/5/98 [POL]	5029	0.53	0.65	0.72	0.49	0.53	0.00	0.46

Date [Site]	Filter #	Fe Normalized	Ni Normalized	Cu Normalized	Zn Normalized	As Normalized	Sn Normalized	Pb Normalized
9/5/98 [POL]	5033	0.42	0.51	0.43	0.51	0.40	0.00	0.34
10/5/98 [POL]	5035	0.27	0.29	0.91	0.47	0.38	0.34	0.29
11/5/98 [POL]	5037	0.65	0.81	0.64	0.92	0.55	0.34	0.36
13/5/98 [POL]	5040	1.04	0.88	1.01	1.01	0.69	0.00	0.85
30/5/98 [POL]	6003	0.92	1.00	0.93	1.76	0.83	0.48	0.86
9/6/98 [POL]	6020	1.04	1.07	0.82	1.21	0.84	0.61	0.79
11/6/98 [POL]	6022	0.75	0.96	0.60	0.79	0.69	0.00	0.53
23/6/98 [POL]	6041	1.00	1.00	1.00	1.00	1.00	1.00	1.00
29/6/98 [DO2]	6050	1.62	0.77	1.56	1.19	0.74	0.40	1.40
6/7/98 [POL]	6057	0.71	0.94	0.64	0.80	0.75	0.41	0.56
12/6/98 [DO2]	6024	1.35	0.97	1.21	1.50	0.75	0.36	1.10
8/5/98 [DO2]	5030	1.07	0.83	1.73	1.08	0.76	1.22	1.50
9/5/98 [DO2]	5032	0.47	0.53	0.84	0.54	0.40	0.29	0.75
10/5/98 [DO2]	5034	0.39	0.52	0.69	1.05	0.35	0.00	0.62
11/5/98 [DO2]	5036	0.81	0.89	1.29	1.49	0.59	0.00	0.77
13/5/98 [DO2]	5041	2.32	1.17	2.83	1.54	0.89	1.45	3.41
30/5/98 [DO2]	6004	1.07	0.96	3.54	1.20	0.92	6.86	1.64
9/6/98 [DO2]	6019	1.62	1.17	1.90	1.36	0.88	0.97	6.34
11/6/98 [DO2]	6021	1.16	1.12	1.36	1.12	0.88	0.63	4.65
29/6/98 [POL]	6049	1.42	0.93	2.19	1.84	0.78	0.59	2.88
23/6/98 [DO2]	6042	1.76	1.36	2.66	2.38	1.36	2.12	3.49
12/6/98 [POL]	6023	1.09	1.01	2.25	0.94	0.76	0.56	0.89
6/7/98 [DO2]	6058	1.03	0.97	1.07	1.11	0.88	0.47	5.29

Date [Site]	Filter #	Ti Normalized	Mn-Sn Metal Index	TPAC (DCM)	R234 (DCM)
14/4/96 [P25]	1491	0.15	0.25	20.60	4.1
13/4/96 [P25]	1492	0.19	0.38	27.70	2.4
12/4/96 [P25]	1493	0.18	0.30	4.00	4.4
9/4/96 [P25]	1494	0.16	1.44	68.80	2.1
5/4/96 [P25]	1495	0.19	0.67	2.50	3.2
6/4/96 [P25]	1496	0.06	0.78	8.70	3.2
11/4/96 [P25]	1497	0.16	3.14	128.00	2.3
10/4/96 [P25]	1498	0.11	3.93	246.00	2.0
8/4/96 [P25]	1499	0.16	1.42	33.30	3.2
7/4/96 [P25]	1500	0.17	1.90	73.00	2.8
/4/96 [P25]	1471	0.20	2.18	45.20	2.0
/4/96 [P25]	1472	0.29	2.49	101.30	2.3
/4/96 [P25]	1473	0.08	9.21	58.10	2.6
25/4/96 [P25]	1378	0.10	1.79	21.40	2.8
24/4/96 [P25]	1379	0.12	0.86	17.90	2.8
24/4/96 [P25]	1379 replicate	0.11	0.79	17.90	2.3
23/4/96 [P25]	1380	0.15	0.92	50.40	2.1
22/4/96 [P25]	1381	0.16	0.70	42.70	2.4
1/5/96 [P25]	1411	0.12	2.86	48.80	2.8
30/4/96 [P25]	1412	0.12	1.73	38.90	2.8
29/4/96 [P25]	1413	0.12	1.95	14.90	2.9
28/4/96 [P25]	1414	0.19	0.80	16.50	2.6
26/4/96 [P25]	1416	0.16	2.85	139.40	2.3
13/5/96 [P25]	1479	0.16	5.32	149.50	2.4
12/5/96 [P25]	1480	0.19	2.48	44.30	3.0
11/5/96 [P25]	1481	0.18	0.37	1.70	2.7
10/5/96 [P25]	1482	0.18	0.67	21.10	3.3
8/5/96 [P25]	1484	0.12	0.59	2.80	2.5
20/4/96 [P25]	1485	0.15	1.79	76.50	2.5
/4/96 [P25]	1486	0.12	1.70	16.20	3.3
18/4/96 [P25]	1487	0.14	0.89	16.60	2.5
17/4/96 [P25]	1488	0.16	3.58	109.80	2.5
16/4/96 [P25]	1489	0.26	2.11	88.10	2.4
15/4/96 [P25]	1490	0.37	0.90	61.30	4.1
5/5/96 [P25]	1503	0.11	0.49	3.40	
4/9/97 [DO1]	1446	0.03	2.58	5.34	3.2
9/9/97 [POL]	1437	0.05	0.28	0.84	4.2
10/9/97 [DO1]	1436	0.07	0.36	1.08	5.1
22/9/97 [DO1]	5002	0.39	0.49	3.02	4.4
29/9/97 [DO1]	5009	0.18	2.23	15.59	2.1
4/9/97 [POL]	1445	0.04	3.43	16.10	2.2
9/9/97 [DO1]	1438	0.05	0.86	2.57	4.8
10/9/97 [POL]	1435	0.05	0.70	2.80	3.9
22/9/97 [POL]	5000	0.42	2.86	6.89	2.8
29/9/97 [POL]	5010	0.20	1.22	8.84	2.5
8/5/98 [POL]	5029	0.56	0.33	0.87	5.2

Date [Site]	Filter #	Ti Normalized	Mn-Sn Metal Index	TPAC (DCM)	R234 (DCM)
9/5/98 [POL]	5033	0.49	0.24	0.35	6.1
10/5/98 [POL]	5035	0.29	0.30	0.20	6.3
11/5/98 [POL]	5037	0.85	0.33	0.37	6.0
13/5/98 [POL]	5040	0.89	1.24	4.29	3.8
30/5/98 [POL]	6003	1.03	0.76	1.10	4.2
9/6/98 [POL]	6020	1.17	0.80	1.32	5.1
11/6/98 [POL]	6022	0.93	0.40	0.70	5.1
23/6/98 [POL]	6041	1.00	1.00	2.73	5.8
29/6/98 [DO2]	6050	0.66	2.02	5.69	5.4
6/7/98 [POL]	6057	0.94	0.42	0.48	5.0
12/6/98 [DO2]	6024	0.91	1.57	3.29	5.1
8/5/98 [DO2]	5030	0.58	1.73	8.92	3.9
9/5/98 [DO2]	5032	0.42	0.39	1.72	4.6
10/5/98 [DO2]	5034	0.44	0.25	0.94	7.7
11/5/98 [DO2]	5036	0.85	0.79	2.48	4.6
13/5/98 [DO2]	5041	0.65	3.50	76.74	3.0
30/5/98 [DO2]	6004	0.81	4.24	2.99	3.9
9/6/98 [DO2]	6019	0.87	2.14	4.59	4.4
11/6/98 [DO2]	6021	1.03	1.28	1.61	4.4
29/6/98 [POL]	6049	0.75	1.38	4.76	4.4
23/6/98 [DO2]	6042	1.18	2.37	3.56	6.9
12/6/98 [POL]	6023	0.89	1.08	2.23	5.0
6/7/98 [DO2]	6058	0.94	0.84	1.61	5.1