

Source Apportionment of Fine and Coarse Particles  
in Southern Ontario, Canada

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## INTRODUCTION

Environment Canada, in cooperation with the Ontario Ministry of Environment and the Walpole Island Indian Band, has been conducting an air monitoring study in a region of southern Ontario near Detroit over concerns about trans-boundary transport of pollutants. Two sampling sites are located in the city of Windsor, Ontario. One Windsor sampling site (WIN1) is centrally located in the city of Windsor at the Ontario Ministry of the Environment monitoring site at 467 University Avenue. This site is only 6 km south of a large municipal waste incinerator operated by the Greater Detroit Resource Recovery Authority (GDRRA) and is also close to other point sources in Detroit. The second Windsor sampling site (WIN2) is located less than 5 km to the southwest of WIN1. WIN2 is closer to the high density of point sources in south Detroit. The Windsor sites are frequently downwind of the numerous emission sources of the greater Detroit area, which include coke ovens, iron and steel industry, incinerators, power generation facilities, lime and cement operations, and automotive assembly plants. The Windsor sites are also influenced by the regional background of secondary sulfate common in the eastern U.S. and Canada, as well as by automobile emissions. A third site was located at Walpole Island, about 55 km to the northeast of the WIN1 site in a rural area. This site (WAL) was chosen to represent background conditions, although this site is also influenced to some degree by primary industrial emissions and secondary pollutants. Locations of sampling sites are shown in Figure 1.

Chemical mass balance source apportionment of fine and coarse particles will be applied to X-ray fluorescence (XRF) data. Meteorological observations and individual particle morphology and composition will be used to interpret the results.

## EXPERIMENTAL

Samples for this analysis were collected during the period from January 30, 1991 - November 26, 1991. Sampling at each site took place for 24 hours from midnight to midnight every 6 days with PM-10 dichotomous samplers having nominal flow rates of 16.7 lpm. Samplers had a cutpoint of 2.5  $\mu\text{m}$  to separate the coarse and fine particles, which were collected on 37-mm diameter Teflon filters. Fine and coarse particle mass concentrations were determined gravimetrically. Elemental concentrations were determined by energy-dispersive XRF at the U. S. EPA, Research Triangle Park facility.

A subset of the samples was selected for analysis by scanning electron microscopy combined with energy-dispersive XRF (SEM/EDX). Morphological features of the particles combined with chemical data have been shown to be useful in resolving source types which cannot be resolved by conventional means.

Meteorological data <sup>was</sup> obtained from the Windsor Airport and from a portable meteorological station at Walpole Island. Average wind speed and prevailing wind direction during each sampling period are used to help interpret particulate concentrations measured.

Locations and emissions of major point sources in the Detroit-metropolitan area (Figure 1) were obtained from the U. S. EPA Region 5 office.

**DATA SUMMARY****General**

Mass and elemental concentrations measured for coarse and fine particles at each site are summarized in Table I. Only those species whose concentrations are at least twice their uncertainty for at least two sets of measurements (either coarse or fine) are reported. In general, concentrations of industrial metals and chlorine (Cl) were higher at the Windsor sites than at the background Walpole site. The particularly high concentration of Cl in the coarse fraction at WIN2 reflects the proximity of WIN2 to the Canada Salt Corporation in Windsor. The tin (Sn) values should be regarded with caution because of the high and variable Sn background observed during the analysis of these samples. Sulfur is the dominant species measured in the fine fraction. It should be noted, however, that XRF does not measure the organic carbon, elemental carbon, or water vapor.

**Comparison of Elemental Ratios for Soil-Related Elements**

The ratios of soil-related elements (Al, K, Ca, Fe) to Si in the fine and coarse fractions from each sampling site are compared with their ratios in crustal limestone and shale profiles from the U. S. EPA's Volatile Organic Compound (VOC)/Particulate Matter (PM) Speciation Data System<sup>1</sup> in Table II. Such a comparison reveals whether these elements have non-crustal sources.

The K/Si ratio in the coarse fraction is relatively constant across the sampling sites with low variability and is very close to the crustal shale value. It is assumed that the dominant source of Si in both the fine and coarse fraction is soil as represented by crustal shale; therefore, soil is likely the dominant source of K and Si in the coarse fraction. In contrast, the K/Si ratio in the fine fraction is quite variable at each site and from site to site, and is much higher than the crustal shale ratio. This indicates a large, non-soil contribution to the fine K.

The Al/Si ratio in the coarse fraction has the lowest variability and is most similar to the crustal value at the WIN2 site. At the WAL site, coarse Al/Si is only a little higher than the crustal value, but is quite variable. The Al/Si ratio at the WIN1 site is much higher than the crustal value and is quite variable. Environment Canada has found high Al values in the coarse fraction at a number of other sampling sites and have attributed this to wear of the dichotomous sampler inlets as a result of leak checking. The Al/Si ratios in the fine fraction are more difficult to interpret because of the large number of fine Al values near the detection limit.

The Ca/Si ratio in the coarse and fine fractions is quite variable at the Windsor sites and is higher than at the Walpole site. All Ca/Si ratios are higher than the crustal shale values. There are several limestone/cement operations within 15 km of the Windsor sampling sites. Fugitive dusts from these operations are likely reaching the Windsor sites and influencing concentrations there. Some of these dusts are probably reaching the Walpole site and influencing concentrations there, although to a lesser extent.

The same pattern observed for Ca/Si ratios is evident for the Fe/Si ratios in the coarse and fine fractions, reflecting the close proximity of the Windsor sites to the steel-related industries of south Detroit. At WAL, the Fe/Si ratio is close to that of crustal shale and the variability is only 28% (lower than at the Windsor sites). There may be little coarse Fe from the steel-related industries reaching WAL, as opposed to fine Fe, which may travel

farther than the coarse Fe. There is evidence of sources of Fe other than soil at WAL, but the evidence is even stronger at WIN1 and WIN2.

#### Fine- and Coarse-Particle Concentrations as Functions of Prevailing Wind Direction and Wind Speed

Fine- and coarse-particle concentrations were examined to determine any relationships with prevailing wind direction or wind speed. Such an examination can offer clues to the sources of pollutants. For the fine fraction, the highest mass concentrations were observed for winds from the south to west corridor, except for some low concentrations when wind speeds were very high. The lowest concentrations occurred when winds had a northerly or easterly component or when wind speeds were high. For the coarse fraction, one would expect an increase in coarse-particle concentrations with an increase in wind speed as a result of soil and other dust being entrained in the air. However, at all sampling sites, the highest coarse-particle loadings were not associated with high wind speeds but were loosely associated with winds from the southwest. This was also true for coarse particle elements associated with the steel industry (e.g., Fe, Mn and Zn).

#### Correlations Among The Elements

Correlations among the elements were examined to identify clusters of mutually correlated elements which may offer clues to their sources. In the fine fraction, three main clusters of elements were observed for WIN2. These are identified with coal combustion (S, Mn, Se, Mass), steel-related industries and manufacturing (Fe, Mn, Zn, Se), and soil and other dust sources (Ca, Si). At WIN1, similar fine-element clusters were observed, with an additional cluster consisting of V and Ni (attributed to oil combustion). At WAL, correlations reveal clusters identified with coal combustion (S, Se, Mass), soil and other dust (Ca, Si, Fe) and mixed industrial sources (K, Br, Cu, Sn, Zn). The fact that Fe appears in the soil-related cluster suggests that Fe from industrial sources is of lesser importance at WAL. The steel-related cluster was much weaker at WAL.

The coarse-particle element correlations show less distinct clusters than was found for fine particles. In general, two main clusters are found at each site - one associated with soil and the other with steel-related industries. The latter was more prominent at the Windsor sites.

#### CHEMICAL MASS BALANCE SOURCE APPORTIONMENT

The U.S. EPA/DRI Chemical Mass Balance Model<sup>2</sup>, version 7 was used to quantitatively apportion chemical species measured at the sampling sites to the major sources contributing to the particulate mass (fine and coarse) at those sites. The chemical mass balance (CMB) model consists of an effective variance least squares solution to a set of linear equations which express each measured chemical species concentration as a linear sum of the contributions of each source to the chemical species. The effective variance solution gives the most weight to source or ambient measurements with the lowest uncertainty estimates. Source contributions are expressed as the product of the abundance of the species as emitted by the source and the total mass concentration contributed by the source. The set of abundances of all species as emitted by each source represents the "source profile" or "source fingerprint". In practice it is not possible to apportion mass to each individual contributing source. Individual sources may be too similar to one another, too numerous, or may not contribute significantly to the total mass loading. Sources are generally grouped together to represent a single "source

category" or "source type". For example, there are many incinerators in the Detroit airshed, but they will be considered together as one incineration source type and represented by a single profile.

In performing a chemical mass balance, it is assumed that: 1) the abundance of each species used in the fitting procedure is known for each source type, and 2) all major sources of each species used in the fitting procedure must be included in the CMB. Other assumptions made for the CMB model are listed in Reference 2.

One of the performance goals of the CMB model is to account for all of the mass, within uncertainties of the measurements involved. A complete apportionment of the PM10 mass measured in this study is made more difficult because no analyses were performed for elemental and organic carbon or for nitrate, all of which could contribute significantly to the PM10 mass. The lack of data for the carbonaceous species affects both the coarse and fine particle fractions. Biological materials (pollens, spores, plant debris) may comprise a significant portion of the coarse particle mass. Organic and elemental carbon are important components of motor vehicle particulate emissions, especially for diesel vehicles. Apportionment of vehicle particulate emissions presents an intractable problem, not only because of the absence of ambient carbonaceous data, but because of the phasing out of tetraethyl lead from the fuel supply. Lead was previously relied upon as a tracer for motor vehicle particulate emissions.

#### Wind Sector Analysis

In applying a CMB analysis to the data, it is assumed that the source compositions remain constant throughout the sampling period and that the same source profiles apply to all sampling periods. In practice, source compositions may vary over time and space due to changing operating conditions, fuel compositions, raw materials, or meteorological conditions. Chemical compositions may vary at a single source or at many sources within a single source category. To compensate for the variability of sources, samples were averaged together to get a study average for each sampling site. For WIN1, two samples were excluded from the average because of elemental outliers. To get more information on the change of source impacts with changing wind direction, samples from adjacent and/or within wind sectors were averaged together according to the density or proximity of upwind point sources and the similarity of samples from adjacent wind sectors, as appropriate for each sampling site. Samples were averaged together as indicated in Table III. Prevailing winds from the Windsor City Airport were applied to the Windsor sampling sites. Wind data applied to the Walpole samples were measured at the site. These averages were computed for both the fine and coarse fractions. The average values for fine and coarse mass are shown in the table.

#### Source Profiles

A combination of profiles available in the literature and in the U.S. EPA Speciation Data System were used to predict ambient species concentrations. Source selection was based on preliminary analyses of the ambient data (wind sector analyses, correlations, comparisons with natural crustal composition) as well as a review of emissions inventories for the Detroit metropolitan area and consideration of the proximity of sources to the sampling sites. Steel manufacturing and related operations dominate the S.E. Detroit area stationary emissions. These operations include limestone processing, coke ovens, steel manufacture blast furnace, and power generation

facilities. An emissions inventory was not available for the Windsor area. Area sources include motor vehicle emissions, wind-blown crustal material, biological particles, and secondary sulfate from power generation.

Coarse Fraction. Preliminary analyses indicate that fugitive dust from steel-related industries could be important contributors to the ambient coarse particle loading, especially at the Windsor sampling sites. An appropriate profile for this source-type was obtained from a study conducted in the S.E. Chicago area<sup>3</sup>. In this work, profiles were developed for samples taken from haul roadways surrounding coal yards, coke yards, and steel yards. The steel yard road (STL) profile was selected to represent these fugitive emissions in the Detroit area. The coal- and coke-yard profiles are dominated by carbon emissions. Subsequent receptor modeling work on S.E. Chicago samples<sup>4</sup> found coal-yard road dust to contribute significantly to both the coarse and fine fractions, but this source-type is comprised largely of carbon, which was not measured in the ambient data. (Attempts at including coke or coal fugitive dust profiles in the CMB resulted in very poor fits of the data). Crustal shale (SHALE) and crustal limestone (LIME) profiles (numbers 43305 and 43304 in the U.S. EPA's Speciation Data System) were chosen to represent the resuspended soil in the airshed. The need for crustal limestone profile is made apparent in the comparison of Ca/Si ratios in the ambient data with the Ca/Si ratio in the crustal shale profile. Lime is used in the steel manufacturing process, and there are several cement or lime operations listed in the emissions inventory for the S.E. Detroit area. The Canada Salt Corporation is located in close proximity to WIN2. High coarse-particle chlorine concentrations, together with SEM micrographs, have confirmed the impact of this source on WIN2. A pure NaCl (SALT) profile was therefore included in the CMB analysis of the coarse fraction.

A preliminary CMB analysis of average WIN1 and WIN2 samples indicated that Zn, Cl, K, Cr, Ti, and Ni were not being predicted well by STL, SHALE, LIME (and SALT for WIN2) profiles in the apportionment. This combination of underpredicted species indicates that incineration may also contribute to the coarse particle loading. Accordingly, an incineration (INCIN) profile (#17105 from the U.S. EPA's Speciation Data System) was included in the analysis. SEM analysis indicates evidence of incineration-derived particles in the coarse fraction.

Fine Fraction. Up to 4 profiles were used to reconstruct the fine particle data. The single most important measured constituent of fine particle mass is sulfur. Previous studies<sup>5,7</sup> have shown sulfur to exist in the form of sulfate plus associated cations ranging from H<sup>+</sup> to NH<sub>4</sub><sup>+</sup>. A single constituent source profile representing sulfur arbitrarily as ammonium sulfate was included to account for a large portion of the fine particle mass. (This will give an approximately 25% higher estimate for sulfate plus cation than if sulfur is represented as sulfuric acid). While this procedure does account for the secondary sulfate, and thus a large portion of the mass, it does not yield any information on the specific source types contributing to the secondary sulfate. A steel-yard road fugitive dust profile for the fine fraction<sup>3</sup> was used to represent the steel industry emissions. Primary stack emissions from the steel-making process are also potential contributors to fine particle mass, but no satisfactory profiles exist. Crustal shale was used to apportion resuspended soil in the fine fraction. This profile was applied successfully to the coarse fraction. Crustal limestone was suitable for the fine fraction. Source characterization data measured at a Philadelphia municipal solid waste incinerator (profile #17105) was used to apportion all incineration emissions in the airshed. While incineration emissions are not expected to make a large contribution to the fine particle

mass, they could contribute significantly to certain toxic elements, such as Ni and Cr. The chemical profile of a Philadelphia oil power plant was used to apportion emissions from oil-fired boilers in the airshed which are used for municipal and industrial power generation in the airshed. Again oil combustion is not expected to contribute significantly to the fine particle mass but may contribute to toxic metal loadings.

#### **CMB Results**

**Coarse Fraction.** Results for the CMB analysis of the coarse particle fraction study averages and wind sector averages are summarized in Table IV. Fitting species were tailored to each sampling site based on source profiles included and which elements were well-predicted by those sources.

On average between 40% and 60% of the coarse fraction was predicted for the WAL samples. As indicated by the preliminary analyses, the WAL coarse fraction is dominated by soil-derived materials. LIME and SHALE together, on average accounted for more than half of the coarse particle mass, and the ratio of LIME to SHALE was around 0.3 on average. SEM analysis of selected filters revealed evidence of biological particles such as plant debris and pollen, which would account for some of the missing mass.

On average between 55% and 70% of the coarse fraction was predicted for the Windsor sites. At these sites, the contribution of steel yard fugitive dust (STL) was also important. The percent contribution of STL on average was 13% at WIN1 and 19% at WIN2, consistent with the close proximity of those types of sources, especially to WIN2. At both sites, the STL percent contribution was highest for wind sectors with a westerly component and falls off rapidly for wind sectors with a northerly or easterly component. The INCIN profile was able to explain most of the Cl and Zn and some of the K. Also, the small amount of coarse S which was explainable was associated with the INCIN source. SEM analysis supports this observation. At WIN2, the highest INCIN estimates were highest for the N-NNE wind sector ( $7.6 \pm 1.8\%$ ), and W sector ( $7.9 \pm 1.8\%$ ), and lowest for the NE-ESE wind sector ( $3.7 \pm 1.0\%$ ). A similar pattern is observed for WIN1. The largest-capacity (83,000 kg/hr) incinerator in the area is the GDRRA refuse-derived fuel facility, located less than 10km north of WIN1 and north-northeast of WIN2. The Central Wayne County Sanitation Authority municipal solid waste incinerator (18,900 kg/hr) is located less than 20 km west of WIN2. There are other incinerators in the area, but most have a much smaller capacity than those specified here. The ratio of LIME to SHALE was higher at the Windsor sites. At WIN2 the ratio was less than 1 for N-ESE winds and was 1.5 or higher for W and WSW winds. The differences are not statistically significant, but there is a trend which points to the S.E. Detroit area as the origin of much of the fugitive limestone dust. At WIN2, salt is a minor contributor to coarse mass but a major contributor to coarse chlorine, which was very high at this site.

**Fine Fraction.** Results for the CMB analysis of the fine particle fraction study averages and wind sector averages are summarized in Table V. Results are similar at 3 sites with the exception that a crustal component was not a significant contributor to the fine mass at the Windsor sites and was therefore excluded from the final CMB apportionments. Fitting species were tailored to each sampling site based on source profiles included and which elements were well-predicted by those sources.

On average, only 56% to 62% of the fine mass was predicted. Reasons for the inability to apportion all of the fine mass include the lack of carbon measurements, which could be a major constituent of missing sources such as

vehicle particulate emissions or fugitive coal or coke dust. In addition, secondary sulfur has been represented as dry ammonium sulfate. Any sulfates present most likely have some amount of water associated with them which could substantially increase the mass. The amount of the increase depends on the form of the sulfate and the relative humidity history<sup>5,8</sup>. SEM results (see below) indicate that sulfur exists in the form of droplets rather than crystals, suggesting the presence of water in association with fine sulfur. There is also some microscopic evidence suggesting some possible hygroscopic minerals.

Sulfur, as represented by dry ammonium sulfate, dominated the fine particle mass, as expected. Its contribution ranged from 46% to 52% of the fine particle mass. The steel yard fugitive dust component increased from just 2.0% at WAL to 7.8% at WIN1 and 13.8% at WIN2. This trend is consistent with the close proximity of WIN2 to the steel industry activities. The incineration contribution estimates likewise increased from 0.9% at WAL to 3.1% at WIN1 to 4.3% at WIN2. Oil combustion was estimated to make a minor contribution to the fine particle loading at each site.

At the Windsor sites, Mn was consistently underpredicted and Fe overpredicted by the STL profile, resulting in an increased  $\chi^2$  (i.e., a poorer fit to the data). This phenomenon is more pronounced at WIN2. The Fe/Mn ratio in the STL fine fraction profile does not represent the ambient data well. In addition, Ca is significantly overpredicted by the STL profile, indicating a problem with its abundance in the profile. Local steel yard samples, as well as steel manufacturing stack emissions, should be collected and analyzed to determine the best steel-related profiles for the airshed.

At all sites, Cl was significantly overpredicted. We frequently see a loss of Cl over time after sample collection. This is presumed to be due to on-going reactions with atmospheric pollutants or volatilization.

#### SCANNING ELECTRON MICROSCOPY AND X-RAY FLUORESCENCE ANALYSIS

A subset of the samples was selected for analysis by scanning electron microscopy combined with energy-dispersive x-ray analysis (SEM/EDX). Particle morphology combined with chemical data is useful in resolving source types which cannot be resolved by conventional means<sup>9</sup>. SEM may also be used to qualitatively infer the presence of species not measured by XRF (e.g., water associated with sulfates, and soot and organic carbonaceous particles, including pollens and spores).

The five samples selected for SEM/EDX analysis are listed in Table VI, along with their measured coarse mass concentration and the prevailing wind conditions during sampling. All samples examined were collected on Teflon filters; thus, there is some interference from the filter matrix, especially for the fine particles. Ideally, coarse-particle samples should be collected on Nuclepore filters for SEM analysis. The coarse fraction was analyzed for the five samples, with 80 to 160 particles analyzed per sample.

About 10% of the fine particles are collected on the coarse-fraction filter with the dichotomous sampler, allowing for the analysis of fine particles on the coarse-fraction filter. Fine particles on one of the filters (WAL, 7/17/91) were examined. Fine particles identified were either sulfate "droplets" or "organic plus sulfur" particles.

The coarse fractions of all samples were dominated by minerals, which typically comprised about 70% by number of the coarse fraction. Fractions



given for each particle type are by number and not mass concentration. Sample WIN1, 8/10/91 was different from the other samples in that it had the highest fraction (29%) of organic particles (almost entirely spores or pollens) and the lowest fraction of minerals (54%). This is the only sample examined which had a northerly component to the prevailing winds. The mass loading of this sample was also quite low ( $6.8 \mu\text{g}/\text{m}^3$ ). Aluminosilicate particles (from soil, clay, road dust) or calcite particles were generally the most abundant class of particles (about 25% to 35%), but there appear to be real differences in mineral composition among the five samples. The WIN2 samples had the highest fraction of calcite particles (about 25%), while the WAL samples had only about 5% calcite particles. The latter was rich in dolomite relative to the other samples. These three samples were rich in quartz particles (about 12%). The 7/17/91 WIN2 sample was unusually rich in salt crystals (primarily NaCl and MgCl). The other WIN2 sample (4/30/91, 33 km/hr winds) and the WAL sample were lowest in salt particles.

The organic category of particles (soot, plant debris, pollens, spores) typically represented 10% to 20% of the coarse fraction, with the aforementioned exception of sample WIN1, 8/10/91. Too few soot particles were observed to note if there were differences in soot content among the samples.

The fraction of coarse particles from industrial sources ranged from 9% to 20% for the samples examined. The WIN1 samples may show higher concentrations of industrial particles than the other three samples, but the lack of statistics makes it difficult to draw conclusions. All samples had remarkably few fly ash particles, although the WAL sample appears to have a higher concentration than the other samples. The 4/30/91 WIN2 sample appears to have an exceptionally high fraction of iron spheres in the smallest size category ( $1.5 - 2.1 \mu\text{m}$ ) as well as several unusual Fe-rich particles assigned to the "industrial other" class, suggestive of iron foundries and steel making. The WIN1 samples had several unusual particles assigned to the "Mg-Cl-Ca-S" class. Other particles rich in some subset of these elements were also found on these samples. The "Mg-Cl-Ca-S" particles were classified as industrial based on their "processed" appearance: rounded and smooth as opposed to rough and crystalline, and sometimes almost a wet appearance. Alternatively, these particles could be highly deliquescent particles of mineral origin. The 8/16/91 WIN1 sample is notable for the presence of phosphorous- and Zn-bearing particles, probably from industrial sources. Although statistics are poor (only 3 particles were classified as Zn-bearing), the SEM observations support the relatively high Zn concentration measured by XRF in this sample.

#### CONCLUSIONS AND RECOMMENDATIONS

Chemical mass balance results are reasonable considering the meteorological conditions and proximity of sampling sites to sources. SEM/EDX analysis of individual particles supported the general conclusions of the CMB analysis and even provided further insight into the origins of the particles collected. Results could be improved upon by doing the following: 1) Include analysis of major species such as elemental and organic carbon and nitrate; 2) Obtain "site-specific" source profiles for major point and area sources; 3) Collect daytime and nighttime 12-hour samples for some portion of the study to obtain information on diurnal variations of sources. Interpretation of results could be facilitated by doing the following: 1) Obtain local emissions inventory data for Canada; 2) Collect coarse samples on Nuclepore filters to reduce sample matrix interference in the SEM analysis; 3) Employ computer-controlled SEM in addition to manual SEM to reduce the amount of time required per analysis and to increase the number of samples and the number of particles

per sample analyzed by SEM.

#### REFERENCES

1. Volatile Organic Compound (VOC)/Particulate Matter (PM) Speciation Data System, Version 1.4, EPA-450/4-91-027, U.S. Environmental Protection Agency, Research Triangle Park, 1991.
2. J.G. Watson, N.F. Robinson, J.C. Chow, et al., "The USEPA/DRI Chemical Mass Balance Receptor Model, CMB 7.0," Environ. Software, 5(1):38-49 (1990).
3. S.J. Vermette, A.L. Williams, and S. Landsberger, Surface Dust Elemental Profiles - Southeast Chicago, Illinois State Water Survey Contract Report 488, Champaign, Illinois, 1990.
4. S.J. Vermette and S. Landsberger, Airborne Fine Particulate Matter (PM<sub>10</sub>) in Southeast Chicago, Illinois State Water Survey Contract Report 525, Champaign, Illinois, 1991.
5. T.G. Dzubay, R.K. Stevens, G.E. Gordon, et al., "A composite receptor method applied to Philadelphia aerosol," Environ. Sci. Technol. 22(1):46-52 (1987).
6. T.G. Dzubay, R.K. Stevens, C.W. Lewis, et al., "Visibility and aerosol composition in Houston, Texas," Environ. Sci. Technol. 16(8):514-524 (1982).
7. R.K. Stevens, T.G. Dzubay, R.W. Shaw Jr., et al., "Characterization of the aerosol in the Great Smoky Mountains," Environ. Sci. Technol. 14(12):1491-1498 (1980).
8. T.L. Vossler and E.S. Macias, "Contribution of fine particle sulfates to light scattering in St. Louis summer aerosol," Environ. Sci. Technol. 20(12):1235-1243 (1986).
9. T.G. Dzubay and Y. Mamane, "Use of electron microscopy data in receptor models for PM-10," Atmos. Environ. 23(2):467-476 (1989).

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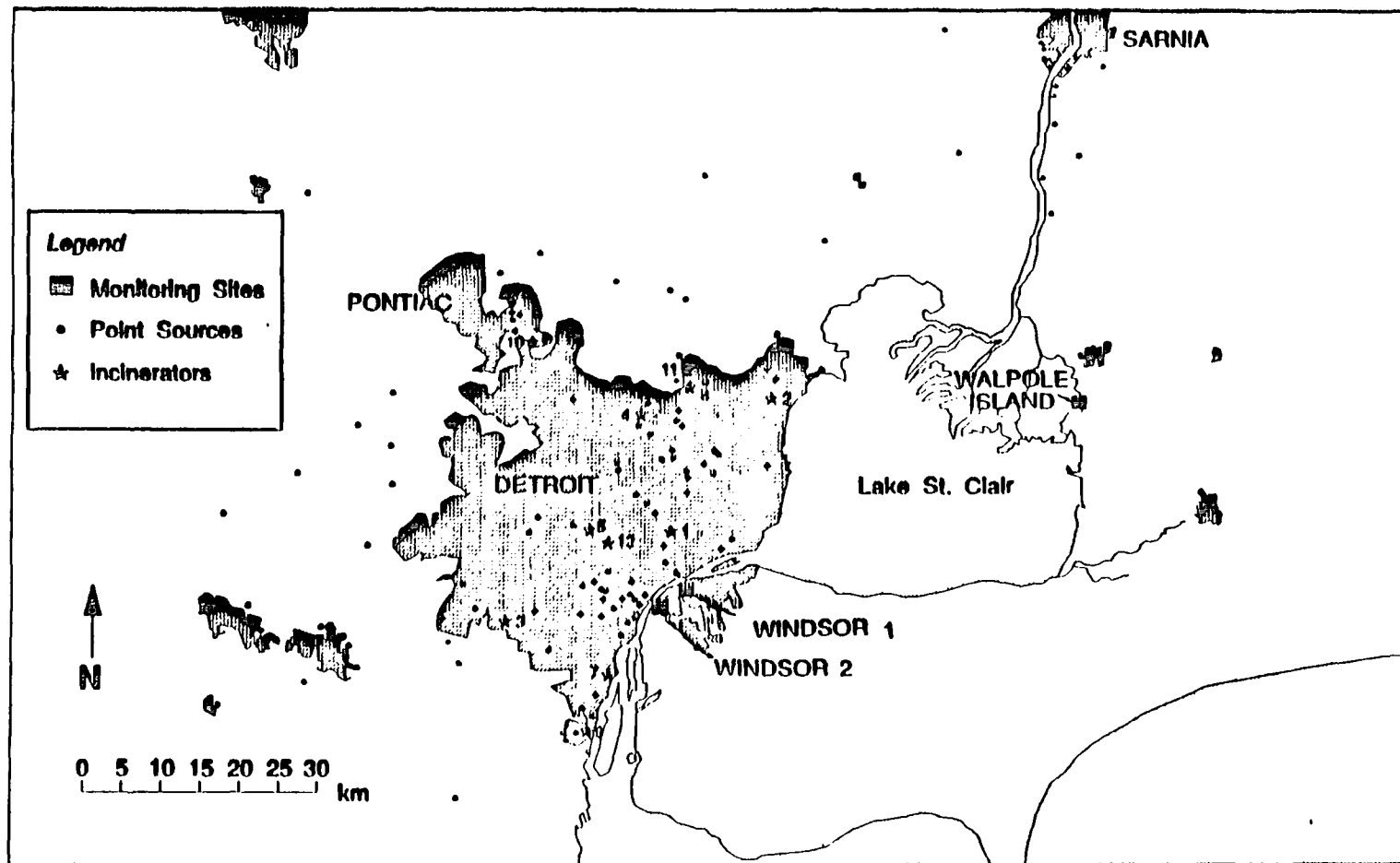


Figure 1. Map of study area showing locations of sampling sites and point sources.

Table I. Average concentrations and uncertainties of elements determined by XRF and mass in the coarse and fine fractions.

	FINE (ng/m <sup>3</sup> )			COARSE (ng/m <sup>3</sup> )		
	WALPOLE	WINDSOR 1	WINDSOR 2	WALPOLE	WINDSOR 1	WINDSOR 2
NUMBER	47	32	47	47	32	47
DATES (1991)	2/5 - 11/26	3/19 - 11/14	1/30 - 11/14	2/5 - 11/26	3/19 - 11/14	1/30 - 11/14
MASS	20,703 ± 832	20,318 ± 851	15,990 ± 779	12,787 ± 749	14,963 ± 766	12,423 ± 701
AL	76 ± 27	129 ± 35	39 ± 24	454 ± 144	1017 ± 304	299 ± 102
SI	107 ± 18	109 ± 19	111 ± 19	1384 ± 347	1298 ± 326	963 ± 244
S	2609 ± 194	2597 ± 193	1818 ± 135	46 ± 71	198 ± 84	174 ± 62
CL	6.1 ± 2.2	9.8 ± 2.5	28.2 ± 3.6	25 ± 4	158 ± 18	250 ± 28
K	74 ± 6	94 ± 7	84 ± 6	140 ± 15	131 ± 15	101 ± 12
CA	44 ± 4	75 ± 6	78 ± 6	652 ± 53	1361 ± 110	1222 ± 99
TI	3.4 ± 2.2	4.3 ± 2.2	3.4 ± 2.4	29 ± 5	33 ± 6	24 ± 4
V	2.0 ± 0.8	2.5 ± 0.8	1.8 ± 0.9	2.1 ± 1.0	2.4 ± 1.0	1.4 ± 0.9
CR	0.6 ± 0.3	0.9 ± 0.4	0.9 ± 0.4	1.0 ± 0.4	2.4 ± 0.6	1.8 ± 0.5
MN	4.6 ± 0.6	13.6 ± 1.1	23.7 ± 1.9	6.7 ± 0.9	15.6 ± 1.7	16.1 ± 1.9
FE	76 ± 7	183 ± 17	258 ± 24	292 ± 31	580 ± 61	581 ± 62
NI	0.8 ± 0.4	0.9 ± 0.4	1.1 ± 0.5	0.6 ± 0.4	1.4 ± 0.5	0.8 ± 0.5
CU	2.7 ± 0.5	9.2 ± 1.1	5.7 ± 0.8	1.5 ± 0.5	7.2 ± 1.1	3.7 ± 0.7
ZN	25.9 ± 2.6	85 ± 8	96 ± 9	10.3 ± 1.6	48 ± 6	42 ± 6
SE	2.5 ± 0.4	2.5 ± 0.4	2.1 ± 0.4	0 ± 0.2	0 ± 0.2	0.1 ± 0.2
BR	3.1 ± 0.5	3.5 ± 0.5	3.1 ± 0.5	0.3 ± 0.3	0.7 ± 0.3	0.6 ± 0.3
SR	0.8 ± 0.3	0.6 ± 0.3	0.8 ± 0.4	2.1 ± 0.4	4.4 ± 0.6	3.8 ± 0.5
SN	8.7 ± 2.8	5.8 ± 2.6	5.5 ± 2.8	2.0 ± 2.5	3.4 ± 2.5	2.6 ± 2.5
BA	4 ± 5	5.1 ± 4.7	7.4 ± 5.0	7 ± 5	12.3 ± 4.8	10 ± 5
PB	11.1 ± 1.4	22.6 ± 2.4	16.2 ± 1.8	1.7 ± 0.8	6.0 ± 1.2	5.0 ± 1.0

Table II. Average ratios (and standard deviations) of soil-related elements to Si.

Site	Size Fraction	Al/Si	K/Si	Ca/Si	Fe/Si
WIN2	Coarse	0.31 ± 0.11	0.12 ± 0.08	1.38 ± 1.01	0.66 ± 0.43
WIN1	Coarse	0.85 ± 1.24	0.11 ± 0.04	1.13 ± 0.31	0.50 ± 0.23
WAL	Coarse	0.38 ± 0.32	0.11 ± 0.04	0.60 ± 0.40	0.23 ± 0.06
WIN2	Fine	0.31 ± 0.34	0.78 ± 0.51	0.70 ± 0.25	2.38 ± 1.58
WIN1	Fine	1.03 ± 1.60	0.96 ± 0.45	0.75 ± 0.26	1.78 ± 0.94
WAL	Fine	0.84 ± 0.85	0.80 ± 0.68	0.47 ± 0.19	0.73 ± 0.38
Crustal Shale	-	0.293	0.097	0.081	0.173
Crustal Limestone	-	0.175	0.112	12.58	0.158

Table III. Wind sector averages applied to Windsor and Walpole samples and the average fine and coarse mass concentrations for those wind sectors.

WALPOLE				WINDSOR 1				WINDSOR 2			
Wind Sectors	No. of Samples	Fine Mass, $\mu\text{g}/\text{m}^3$	Coarse Mass, $\mu\text{g}/\text{m}^3$	Wind Sectors	No. of Samples	Fine Mass, $\mu\text{g}/\text{m}^3$	Coarse Mass, $\mu\text{g}/\text{m}^3$	Wind Sectors	No. of Samples	Fine Mass, $\mu\text{g}/\text{m}^3$	Coarse Mass, $\mu\text{g}/\text{m}^3$
All	40	20.7	12.8	All (minus 2 outliers)	32	20.3	15.0	All	47	16.0	12.4
NNE-ESE	8	14.7	10.0	NNE-E	6	9.8	9.9	NE-ESE	8	7.6	7.2
NNW-N	4	5.1	6.3	N-NNW	3	15.5	11.2	N-NNE	4	12.3	8.3
WNW-NW	5	11.0	10.2	WNW-NW	3	10.9	10.9	WNW-NNW	7	8.8	9.1
W-WSW	16	16.6	11.4	W-SW	10	24.6	21.8	W	4	20.2	12.6
SW	4	25.2	14.1	SSW-S	10	26.6	14.1	WSW	9	19.0	19.1
(SSW-SE)	3	not used	not used					SW-S	15	21.8	13.8
No Data	7										

Table IV. CMB results for coarse-particle fraction given in percent of measured mass with uncertainty estimates.

	SOURCE CATEGORY <sup>4</sup>				
	STL	SALT	INCIN	LIME	SHALE
WAL <sup>1</sup> , AVG	0%	0%	0%	13.7 ± 2.0%	43.3 ± 3.6%
WAL, NE-ESE	0%	0%	0%	17.5 ± 2.4%	40.8 ± 3.5%
WAL, NNW-N	0%	0%	0%	22.3 ± 2.9%	37.5 ± 3.5%
WAL, WNW-NW	0%	0%	0%	14.4 ± 2.1%	50.9 ± 4.1%
WAL, WSW-W	0%	0%	0%	8.5 ± 1.2%	31.2 ± 2.6%
WAL, SW	0%	0%	0%	15.4 ± 2.2%	42.3 ± 3.5%
WIN <sup>2</sup> , AVG-2	13.3 ± 2.3%	0%	6.3 ± 0.9%	20.6 ± 3.5%	21.7 ± 4.0%
WIN1, NNE-E	5.2 ± 1.7%	0%	3.9 ± 0.6%	28.8 ± 4.1%	26.1 ± 3.9%
WIN1, N-NNW	7.9 ± 1.9%	0%	6.7 ± 1.0%	21.1 ± 3.3%	23.2 ± 4.1%
WIN1, WNW-NW	14.0 ± 2.1%	0%	3.5 ± 0.5%	16.0 ± 2.9%	21.3 ± 3.4%
WIN1, W-SW	13.2 ± 2.1%	0%	7.2 ± 1.0%	18.0 ± 3.2%	17.0 ± 3.7%
WIN1, SSW-S	17.4 ± 2.8%	0%	5.8 ± 0.8%	20.7 ± 3.8%	26.4 ± 4.4%
WIN <sup>3</sup> , AVG	19.2 ± 2.8%	1.5 ± 0.6%	6.6 ± 1.6%	20.8 ± 3.8%	17.7 ± 4.1%
WIN2, NE-ESE	5.5 ± 1.8%	1.2 ± 0.4%	3.7 ± 1.0%	26.7 ± 3.9%	30.4 ± 4.1%
WIN2, N-NNE	16.6 ± 2.4%	4.7 ± 1.1%	7.6 ± 1.8%	13.9 ± 2.8%	12.7 ± 3.8%
WIN2, WNW-NNW	20.9 ± 2.9%	1.5 ± 0.7%	7.0 ± 1.7%	21.7 ± 4.0%	17.9 ± 4.3%
WIN2, W	21.3 ± 2.8%	4.1 ± 1.0%	7.9 ± 1.8%	16.4 ± 3.4%	10.3 ± 3.7%
WIN2, WSW	19.7 ± 2.8%	2.4 ± 0.7%	5.5 ± 1.4%	23.5 ± 4.2%	15.5 ± 3.6%
WIN2, SW-S	21.4 ± 3.0%	0%	6.6 ± 0.9%	19.0 ± 3.7%	19.5 ± 3.8%

<sup>1</sup>Chi<sup>2</sup> = 0.18 - 1.40; Degrees of Freedom = 5

<sup>2</sup>Chi<sup>2</sup> = 0.56 - 2.11; Degrees of Freedom = 4

<sup>3</sup>Chi<sup>2</sup> = 0.19 - 1.17; Degrees of Freedom = 5 (except 6 for SW-S)

<sup>4</sup>STL = Steel-yard road dust; SALT = sodium chloride; INCIN = incineration emissions; LIME = crustal limestone; SHALE = crustal shale

Table V. CMB results for fine-particle fraction given in percent of measured mass with uncertainty estimates.

	SOURCE CATEGORY <sup>4</sup>				
	STL	AMSF	OILPP	INCIN	SHALE
WAL <sup>1</sup> , AVG	2.0 ± 0.2%	51.7 ± 6.5%	0.2 ± 0.1%	0.9 ± 0.1%	1.5 ± 0.4%
WAL, NE-ESE	2.0 ± 0.2%	56.4 ± 7.0%	0.5 ± 0.1%	0.7 ± 0.1%	1.4 ± 0.4%
WAL, NNW-N	3.7 ± 0.4%	36.8 ± 4.6%	0.3 ± 0.4%	1.0 ± 0.2%	2.1 ± 0.7%
WAL, WNW-NW	2.2 ± 0.2%	42.2 ± 5.3%	0.2 ± 0.1%	1.4 ± 0.2%	1.7 ± 0.4%
WAL, WSW-W	2.3 ± 0.3%	49.5 ± 6.2%	0.2 ± 0.2%	0.8 ± 0.1%	3.0 ± 0.6%
WAL, SW	2.3 ± 0.2%	49.4 ± 6.2%	0.2 ± 0.1%	0.9 ± 0.1%	1.6 ± 0.4%
WIN1 <sup>2</sup> , AVG-2	7.8 ± 0.7%	52.1 ± 6.5%	0.2 ± 0.1%	3.1 ± 0.3%	0%
WIN1, NNE-E	5.7 ± 0.6%	50.5 ± 6.3%	0.8 ± 0.2%	2.2 ± 0.2%	0%
WIN1, N-NNW	5.6 ± 0.5%	46.1 ± 5.8%	0.6 ± 0.1%	2.6 ± 0.3%	0%
WIN1, WNW-NW	6.0 ± 0.6%	38.5 ± 4.8%	0.1 ± 0.2%	2.2 ± 0.2%	0%
WIN1, W-SW	9.1 ± 0.8%	55.3 ± 6.9%	0.1 ± 0.1%	3.1 ± 0.3%	0%
WIN1, SSW-S	7.5 ± 0.6%	52.3 ± 6.5%	0.1 ± 0.1%	3.4 ± 0.3%	0%
WIN2 <sup>3</sup> , AVG	13.8 ± 1.2%	45.9 ± 5.8%	0.3 ± 0.1%	4.3 ± 0.5%	0%
WIN2, NE-ESE	6.4 ± 0.7%	42.0 ± 5.3%	0.7 ± 0.3%	1.6 ± 0.2%	0%
WIN2, N-NNE	10.7 ± 0.9%	39.9 ± 5.0%	1.2 ± 0.2%	3.7 ± 0.5%	0%
WIN2, WNW-NNW	10.0 ± 0.9%	35.1 ± 4.4%	0.7 ± 0.3%	5.1 ± 0.6%	0%
WIN2, W	10.4 ± 0.9%	31.4 ± 4.0%	0.2 ± 0.1%	3.5 ± 0.4%	0%
WIN2, WSW	17.4 ± 1.4%	51.4 ± 6.4%	0.1 ± 0.1%	5.8 ± 0.7%	0%
WIN2, SW-S	14.3 ± 1.1%	50.4 ± 6.3%	0.1 ± 0.1%	4.0 ± 0.5%	0%

<sup>1</sup>Chi<sup>2</sup> = 0.88 - 3.48; Degrees of Freedom = 5

<sup>2</sup>Chi<sup>2</sup> = 1.37 - 4.67; Degrees of Freedom = 6

<sup>3</sup>Chi<sup>2</sup> = 1.00 - 4.13; Degrees of Freedom = 7

<sup>4</sup>STL = Steel-yard road dust; AMSF = ammonium sulfate; OILPP = oil-fired power plant emissions; INCIN = incineration emissions; SHALE = crustal shale

Table VI. Coarse fraction samples analyzed by SEM/EDX and the coarse mass concentrations and prevailing wind conditions.

Sampling Site	Sampling Date	Coarse Mass, $\mu\text{g}/\text{m}^3$	Prevailing Wind Direction	Mean Wind Speed, km/hr
WAL	7/17/91	19.8	WSW	15
WIN1	8/10/91	6.8	NNW	12
WIN1	8/16/91	23.4	SSW	14
WIN2	4/30/91	36.4	WSW	33
WIN2	7/17/91	30.3	WSW	17



**TECHNICAL REPORT DATA**

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16. ABSTRACT  Environment Canada, in cooperation with the Ontario Ministry of Environment and the Walpole Island Indian Band, has been conducting an air monitoring study in a region of southern Ontario near Detroit. Two sampling sites are located in the city of Windsor, Ontario. The Windsor sites are frequently downwind of the numerous emission sources of the greater Detroit area, which include coke ovens, iron and steel industry, incinerators, power generation facilities, lime and cement operations, and automotive assembly plants. The Windsor sites are also influenced by the regional background of secondary sulfate common in the eastern U.S. and Canada, as well as by automobile emissions. A third site, located on Walpole Island, was set up to assess the background particulate composition, although this site is also influenced to some degree by primary industrial emissions and secondary pollutants.  Fine and coarse particle samples were collected on Teflon filters with a dichotomous sampler. Samples were analyzed by energy-dispersive X-ray fluorescence (XRF) at the U.S. EPA, Research Triangle Park facility. A subset of the samples were selected for analysis by scanning electron microscopy combined with energy-dispersive XRF (SEM/EDX). Morphological features of the particles combined with chemical data have been shown to be useful in resolving source types which cannot be resolved by conventional means. Source apportionment of fine and coarse particles based on SEM/EDX and on conventional (i.e., statistical) methods applied to XRF data will be reported. Meteorological observations will be used to interpret the results.		13. TYPE OF REPORT AND PERIOD COVERED Work Performed December 1991 - June 1993, Proceedings of AWMA Conference - June 1993
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