# Characterization of Emissions From the Eco Waste Solutions Thermal Waste Oxidizer Burlington, Ontario

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## ACKNOWLEDGEMENTS

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# 1. INTRODUCTION

In cooperation with the National Office of Pollution Prevention, the Emissions Research and Measurement Division (ERMD) conducted characterization of the Eco Waste Oxidizer manufactured by Eco Waste Solutions of Burlington, Ontario. The Eco Waste Oxidizer uses a two-step thermal oxidation process. In the first step, municipal solid waste is burned in the dual primary chambers under starved oxygen conditions and relatively low temperatures (500 to 650°C) in order to preserve metal and glass for later recycling. Each of the two primary chambers in this oxidizer has a capacity of two tonnes of waste. Once the waste starts burning, the process becomes self-fuelling until the volume is reduced by over 90 percent. In the second step, smoke and gases from the two parallel primary chambers are treated in the afterburner or secondary chamber at an operating temperature of 1000°C and a minimum of 2 seconds residence time to ensure complete oxidation of the combustion products.

The Eco Waste Oxidizer is configured to treat the flue gases from the afterburner in a water quench system followed by a packed tower scrubber to remove acid gases and metals. However, the scrubber system was bypassed in this study. The main purpose of this study was to characterize the emissions from a well-operated incinerator without control technology.

The Emissions Research and Measurement Division (ERMD) conducted source testing at this facility for various target compounds. These pollutants included particulate, metals, acid gases, dioxins and furans (PCDDs/PCDFs), polycyclic aromatic hydrocarbons (PAHs), selected chlorobenzenes (CBs), octachlorostyrene (OCS), volatile organic compounds (VOCs) and flue gases ($CO_2$, $O_2$, CO, $SO_2$ and $NO_x$). The semi-volatile and volatile organic compounds included Track 1 and CEPA toxic compounds.

## 2. SAMPLING SITE AND LOCATION

Sampling was conducted on the stack exhaust located above the roof of the Eco Waste facility. Samples were extracted from the two existing ports. The sampling location is illustrated in Figure 1. Sampling was conducted from two 4-inch ports positioned approximately 36 inches above the temporary platform and 15 feet above the roof. The stack sampling location met the "eight and two" criteria.

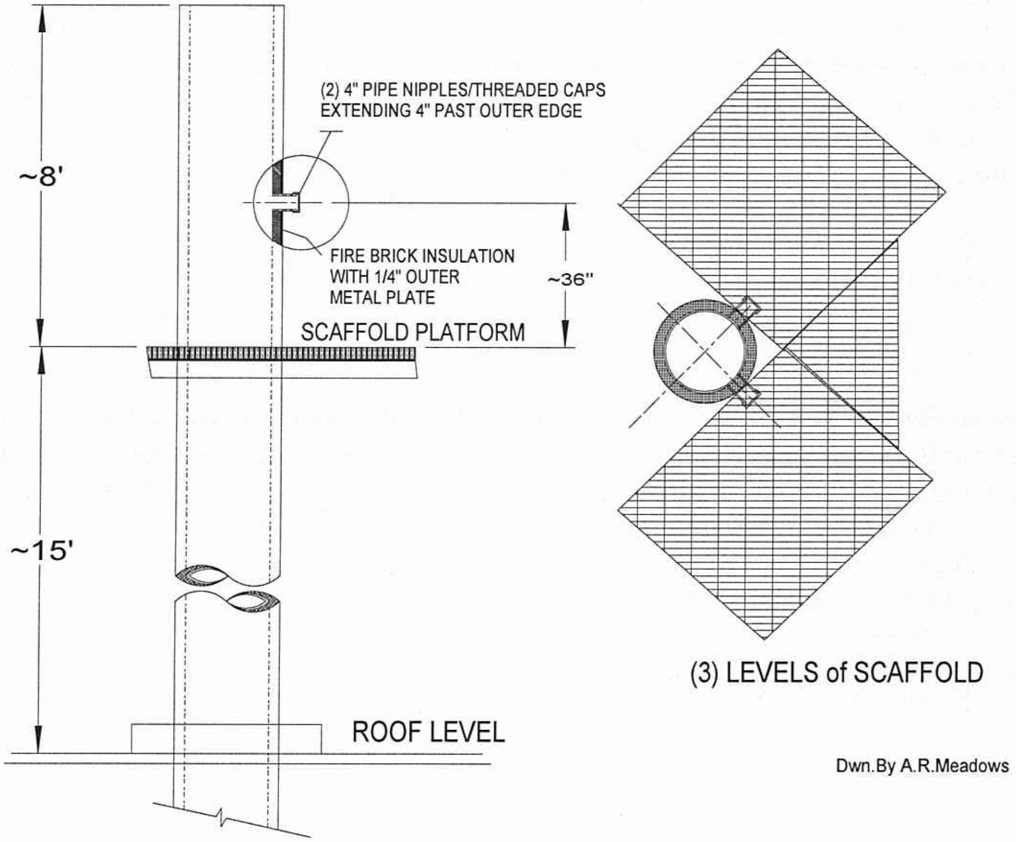


**Figure 1 Sampling Location – Eco Waste Solutions Oxidizer**

## 3. SAMPLING METHODS

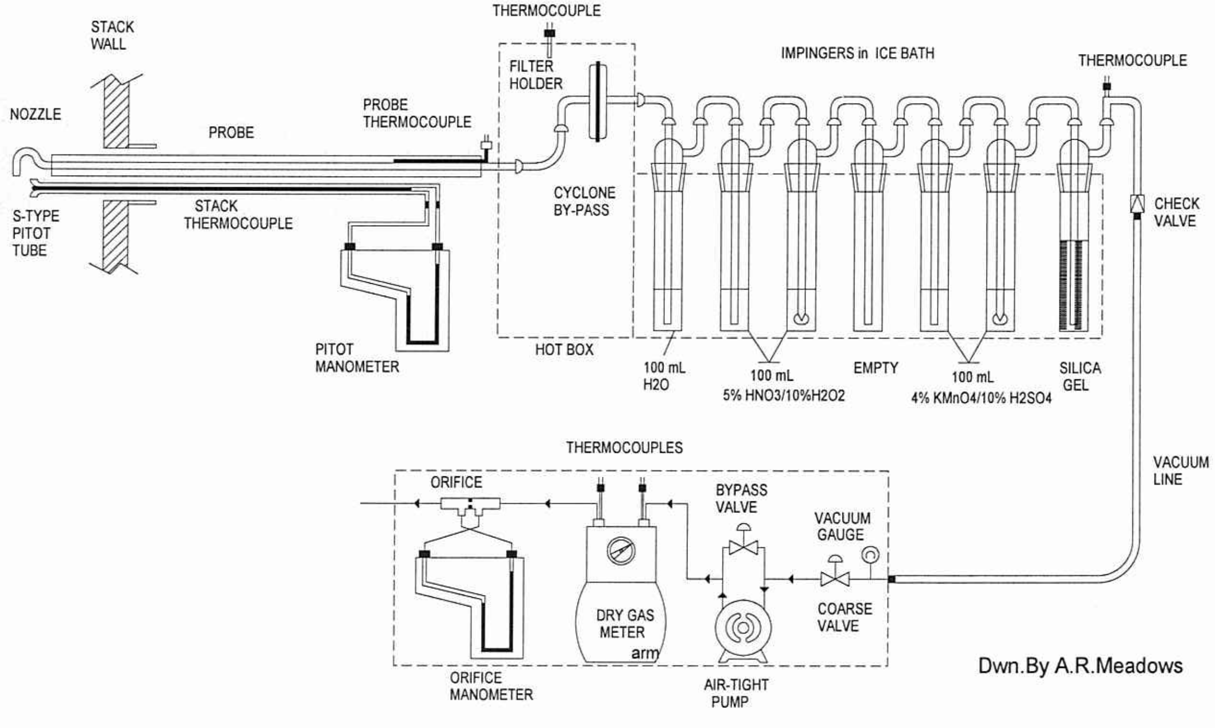
### 3.1 General

The Method 5 train formed the basis of the manual methods used to collect particulate, acid gases, metals and semi-volatile organics during the sampling phase. The train consisted of a probe, heated filter enclosure, leak-free vacuum line, vacuum gauge, flow control valves, vacuum pump and a dry gas and orifice meter. Stack gas and orifice pressures were measured with an inclined manometer and micromanometer. Temperatures were measured in the hot box, impinger train outlet and at the inlet and outlet of the dry gas meter. In the case of the SVOCs, the temperature was also monitored at the Amberlite XAD-2 inlet. All trains were assembled in the ERMD mobile lab.

Leak-checks were conducted at the beginning and at the end of each run or whenever a train joint was opened. Sampling was conducted from two traverses at isokinetic sampling rates with readings recorded every five minutes. Sampling duration for the particulate/metals and organic runs was 2 and 4 hours respectively.

### 3.2 Particulate/Acid Gases/Metals Train Description

EPA Method 29, "Determination of Metal Emissions from Stationary Sources", was used to determine particulate and metal emissions. Particulate emissions were collected in the probe and on the heated filter. The condensation and collection of the gaseous fraction was accomplished using seven impingers connected in series. The first impinger was filled with 100 mL deionized water to trap acid gases, followed by two impingers containing 100 mL of an acidic solution of hydrogen peroxide (5% $HNO_3$/10% $H_2O_2$), followed by an empty impinger, followed by two impingers containing 100 mL each of an acidic solution of potassium permanganate (4% $KMnO_4$/10% $H_2SO_4$) and finally followed by a silica gel impinger. A schematic of the sampling train is shown in Figure 2.



Dwn.By A.R.Meadows

**Figure 2 Particulate/Acid Gases/Metals Sampling Train**

The glassware was pre-cleaned following the meticulous procedure detailed in the method. Eight samples from each test were obtained from the recovery procedure and submitted for analysis. These samples include the particulate filter, aliquots of the first impinger water, rinses of the front- and back-half glassware with various portions of acetone, nitric acid, acidified potassium permanganate and hydrochloric acid that are detailed in the method. As well, aliquots of the reagents used in the sampling train and in the recovery procedure were submitted for blank analysis.

Glass bottles with Teflon-lined caps were used for storage of acidified $KMnO_4$ containing samples and blanks. No metal components were used in this method. In its place, Teflon probe fittings and filter supports and quartz nozzles and probes were utilized to avoid contamination of the train and samples.

### 3.3 SVOC Train Description

The Environment Canada Report EPS 1/RM/2 *"Reference Method for Source Testing: Measurement of Releases of Semi-volatile Organic Compounds from Stationary Sources"* was used to determine the emissions of dioxins, furans, polycyclic aromatic hydrocarbons, chlorobenzenes and octachlorostyrene from the stack. A schematic of the sampling train is shown in Figure 3.

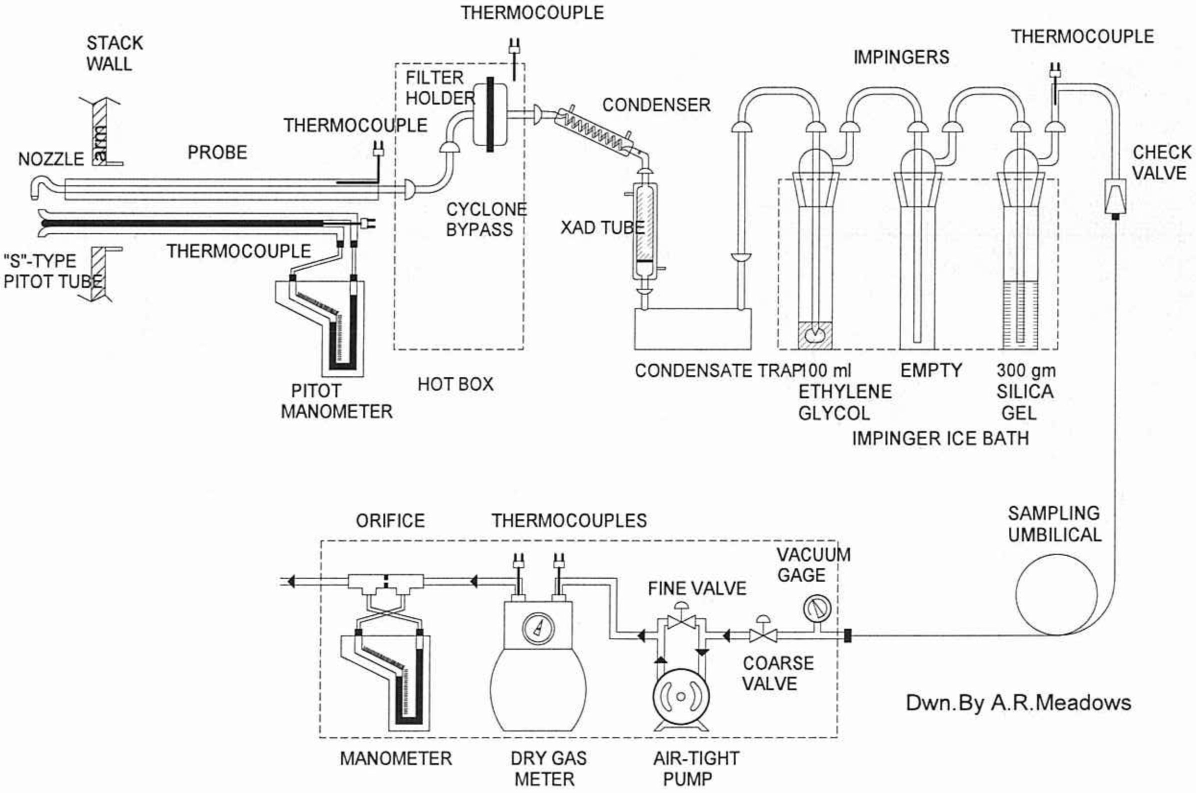


**Figure 3 Dioxin, Furan, PAH, CB and OCS Sampling Train**

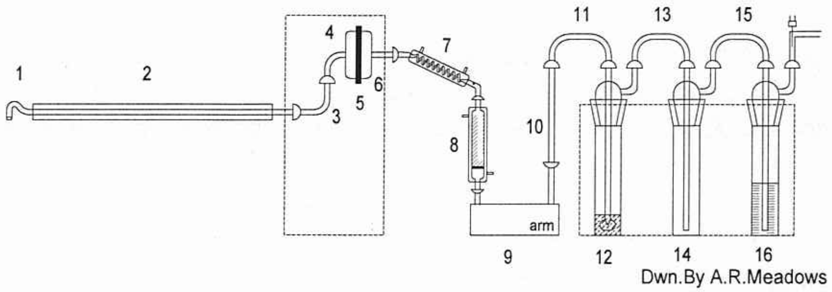
This method is the most widely accepted for the measurement of organic compounds with boiling points above 100°C. Gaseous organics were trapped in a single adsorbent tube containing about 40 grams of Amberlite XAD-2 resin. As the temperature of the resin must be kept below 20°C for optimal collection efficiency, the hot gases leaving the filter enclosure were cooled by passing them through a condenser cooled with ice bath water. The tube containing the XAD-2 resin was also water-cooled. Condensate formed in the cooling coil percolated through the resin bed and was collected in a condensate trap. An impinger containing ethylene glycol inserted downstream of the Amberlite acted as a back-up collection media in the event of breakthrough of organics through the resin. The resin tube was covered with aluminum foil during sampling and storage to prevent photodegradation of the trapped organics. All glassware joints were wrapped with Teflon tape as vacuum greases are not permitted for organic sampling. Sampling duration was four hours. Quartz nozzles and liners were used in the sampling train.

### 3.3.1 Glassware Cleaning and Proofing

Prior to the test program, all train glassware, probe brushes, glass wool and aluminum foil were cleaned following the rigorous procedure in the Reference Method. The glassware cleaning procedures were verified by analyzing the proofing rinses of the sampling trains. Pre-cleaned and proofed commercial sample storage bottles were used for this test. Four complete sets of train glassware were prepared for this survey. The XAD-2 was pre-cleaned and analyzed for contamination prior to the survey. All reagents were distilled-in-glass grade. Details of the cleaning and proofing procedures are given in Report EPS 1/RM/2.

### 3.3.2 Sample Recovery

Following the completion of each run, the organic train was recovered in the ERMD mobile laboratory. During the transportation between the sampling site and the lab, all openings were sealed with pre-cleaned glass plugs or caps or aluminum foil. The recovery procedures involved the brushing and rinsing of the train components with acetone and hexane. Only Teflon wash bottles were used during sample recovery. The loaded filter was carefully removed from the holder, sealed in pre-cleaned foil and stored in a pre-cleaned glass petri dish. Amberlite tubes were capped and re-wrapped in aluminum foil. Liquid samples were stored in pre-cleaned amber bottles to prevent photodegradation of the organics. Bottle lids were lined with Teflon. All samples were kept refrigerated following recovery. The sample recovery procedures are detailed in Figure 4. All samples were forwarded to the Analysis and Air Quality Division (AAQD) of Environment Canada for organic analysis.



| Sample | Component(s) | Recovery Procedure |
|---|---|---|
| 1 | 1,2,3,4 | Wash and brush 3 times each with acetone (A) and hexane (H). Rinse 3 times each with A and H. |
| 2 | 5 | Remove filter carefully from filter holder. Place on pre-cleaned foil. Fold in half and crimp the foil edges. Place in pre-cleaned petri dish. Seal petri dish. |
| 3 | 6,7 | Soak 5 minutes each with A and H. Rinse 3 times each with A and H. |
| 4 | 8 | Cap ends and wrap in foil. |
| 5 | 9,10,11,12 | Empty contents into container and rinse 3 times with HPLC water. |
| 6 | 6 to 15 except 8 | Rinse three times each with A and H. |

*Mark liquid levels on all bottles and wrap all the caps with tape.*
*All sample containers are pre-cleaned amber glass bottles with pre-cleaned Teflon lid liners.*

**Figure 4 Recovery Procedure for Dioxins, Furans, PAHs, CBs and OCS**

In addition to the regular sampling trains, a blank train was assembled for the tests. The blank train was treated in the same manner as the sampling trains except that no stack gases were sampled. However, a volume of ambient air, equal to that drawn during the leak checks was drawn through the blank train. Essentially, the blank train serves as a check for background levels of organics originating from ambient air, handling of train glassware and rinsing agents.

### 3.4 Volatile Organic Compounds (VOCs)

VOCs are classified as those organics having saturated vapour pressures at 25°C greater than $10^{-1}$ mm Hg. The method is based on the collection of a gaseous sample in a previously cleaned, verified and evacuated 6-liter, stainless-steel canister. The canister's interior surface is covered by pure chrome-nickel oxide which is formed during the SUMMA® passivating process. This vessel provides a stable sample collection and storage media for many organic compounds.

A modified method TO-14 *(Compendium Method TO-14 Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. EPA, May 1988)* was used as the basis for the VOC sampling train. The train consisted of a stainless-steel probe connected by Teflon tubing to the canister. The gases were drawn by a Teflon-coated pump through a critical orifice (hypodermic needle) into the canister (Figure 5).

Two canisters were collected for each SVOC run corresponding to the first and second halves of the traverses. Sampling duration for the VOC samples was variable, ranging from 50 to 70 minutes. The sample was collected into the evacuated canister to a final pressure of 18 to 19 psig. Following sample collection, the canister valve was closed and the canisters were transported to the AAQD laboratory for analysis.

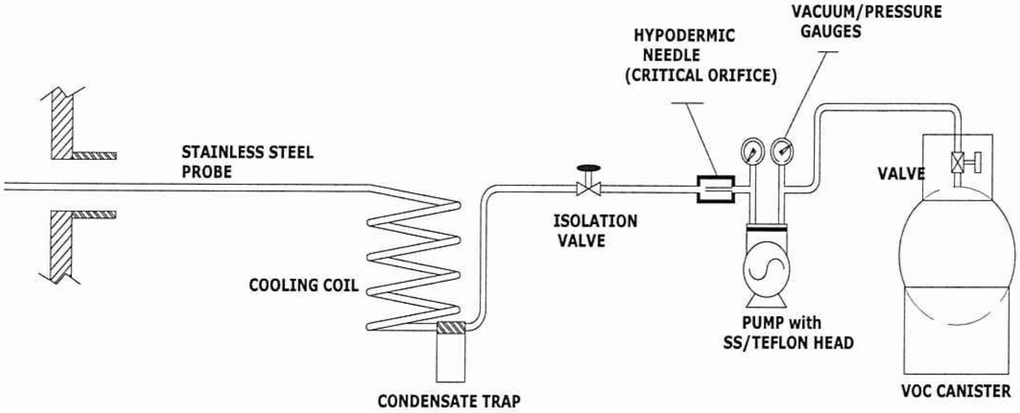


**Figure 5 Volatile Organic Compounds Sampling Train**

## 3.5 Flue Gases

An integrated gaseous sample method was employed to collect a representative sample from the stack. This was accomplished by drawing sample gas through a 30-inch Inconel probe located directly in the exhaust stream. Following particulate removal in a heated filter and conditioning (drying and cooling) of the sample gas, the sample gas was drawn through a stainless steel/Teflon head pump into a high volume aluminized Tedlar sample bag. A sampling rate of 1 liter per minute was used over a 30-minute sampling period per sample. A schematic of the system is shown in Figure 6.

Each integrated sample was then analyzed using both an ECOM Model KD (electrochemical analysis of $O_2$, CO, $SO_2$ and NO and $NO_2$) and a Nova Model 306 BD (infrared analysis of $CO_2$), to determine target species concentration. Each instrument was individually calibrated twice a day using two ranges of certified gas standards. Initial calibration was carried out prior to the commencement of sampling, once all equipment had reached operating conditions, while final calibration was performed at the end of sampling.

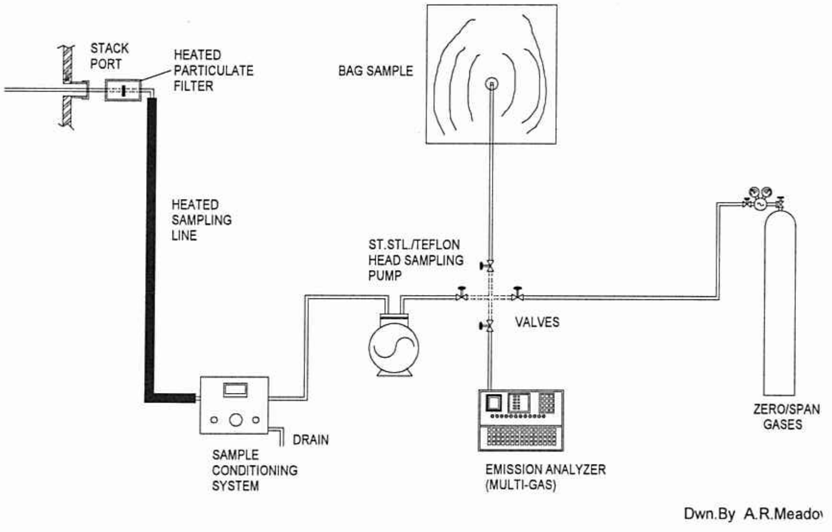


**Figure 6 Flue Gas Monitoring System**

# 4. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

All stack sampling equipment was calibrated prior to sampling using accepted techniques. Items that were calibrated included:

- Dry Gas Meter ($\gamma$)
- Orifice ($K_0$)
- Pitot Tubes ($C_p$)
- Barometers ($P_{bar}$)
- Inclined Gauges ($\Delta p$)
- Nozzle Diameters ($N_d$)
- Temperature Readers (T)

The dry gas and orifice meters were calibrated using a spirometer. Pitot tubes were calibrated at the National Research Council wind tunnel. Barometers and inclined gauges were calibrated against a standard reference mercury barometer and an inclined manometer respectively. Thermocouple readers were calibrated using an ice bath and boiling water. Nozzle openings were measured by averaging three measurements with a vernier caliper. In addition to the above, the sampling consoles and inclined gauges were checked for leaks and the operation of all probe and box heaters was verified.

# 5. ANALYTICAL METHODS

## 5.1 Particulate and Metals

Particulate was determined gravimetrically following desiccation of the front-half acetone rinse and loaded filter. Acid gases were determined by ion chromatography analysis of the first impinger contents. Chloride and fluoride were expressed as HCl and HF. The samples were acid digested, and appropriate fractions were analyzed for mercury by cold vapour atomic absorption spectroscopy (CVAAS) and the remainder of the metals was analyzed by inductively coupled argon plasma emission spectroscopy (ICAP). The front- and back-half components were analyzed separately.

## 5.2 Semi-volatile Organic Compounds

Upon receipt in the laboratory the samples were inspected to ensure integrity and proper labeling. The samples were then entered into the laboratory information management system (LIMS) where they were assigned a laboratory code. The code was then entered onto each of the containers which were then stored in a fridge at 4°C until sample processing proceeds.

Typically the train samples are divided into the front-half (probe rinse, filter, and front-half filter holder rinse) and back-half sections (back-half filter holder rinse, XAD, condensate trap, glycol impinger and back-half glassware rinses). The solvent fractions were dried by passage through sodium sulphate and reduced in volume by rotary evaporation. The solids (filter and XAD) were air dried prior to a 20-hour soxhlet extraction using cyclohexane/toluene (8:2 v/v). Prior to extraction, each sample was spiked with a solution containing a known amount of carbon-13 labelled dioxin/furans and chlorobenzenes as well as deuterated PAH. These were used to assess losses incurred during the extraction and sample cleanup procedures. Analytical results for dioxin/furan and chlorobenzenes/octachlorostyrene were corrected for the recovery of these surrogates. PAH results were not corrected for surrogate recovery.

After extraction, the solvent extracts of the solids were reduced in volume and combined with the train rinses prior to cleanup. The samples were split into two equal fractions. One fraction was used for PAH cleanup and analysis while the other was used for dioxin/furan and chlorobenzene/octachlorostyrene cleanup and analysis.

The PAH cleanup involved passing the sample extract through an activated silica column. Co-extracted compounds which may cause interference during analysis were eluted out of the column while the PAHs were retained on the column. A more polar solvent was then applied to the column to elute the PAHs. The cleaned sample extract was concentrated to 500 μL and an internal standard was added to monitor instrumental performance and was used to correct for any variations in injection and sample volume. The sample was analyzed using low resolution mass spectroscopy. Calibration standards containing various known amounts of the analytes were injected into the instrument before, during and after the samples were injected. These standards were used to determine the concentrations of the analytes in the sample. The accuracy of the standards was periodically assessed using standard reference materials.

The dioxin/furan and chlorobenzene/octachlorostyrene cleanup is more rigorous since the concentrations of the dioxin/furans are much lower than other compounds that may be present in the extract. These co-extractants could interfere with the final analysis. Initially the sample extract was passed through a multi-bed silica column containing layers of acid, base and silver nitrate. Some of the co-extractants were retained on the column and others may be reduced or oxidized. Sulphur containing compounds were removed by the silver nitrate. The extract was then passed through an alumina column to separate out the dioxin/furans from other compounds such as PCBs and chlorobenzenes/octachlorostyrene. The fraction containing the chlorobenzenes/octachlorostyrene was reduced to 500 μL and an internal standard was added to monitor instrumental performance and to correct for any variations in injection and sample volume. The sample was analyzed using low resolution mass spectroscopy. The fraction containing dioxin/furans was reduced to 20 μL and an internal standard was added to monitor instrumental performance and to correct for any variations in injection and sample volume. The sample was analyzed using high resolution mass spectroscopy.

As a part of quality assurance and quality control, a method blank is usually processed along with the samples to assess cross contamination. A control sample, usually a standard reference material containing a known amount of analytes, may also be processed along with the samples to check extraction, cleanup and analytical efficiency. The division also participates in inter-laboratory studies. The results of these studies are used to compare the results obtained in-house with the results obtained from several different laboratories. These studies involve various analytes from a variety of matrices. The division is accredited by CAEAL for the analysis of PAH and dioxin/furan.

## 5.3 Volatile Organic Compounds

The stack samples in canisters were analyzed using thermal desorption technique with a high-resolution gas chromatograph and quadrupole mass-selective detector (GC-MSD) as described in EPA Methods TO-15 and TO-17. A Dynatherm Analytical Instruments ACEM Model 900 thermal desorption system was used for sample preconcentration. Sorbent tubes packed with 20/35 mesh Tenax-TA, 60/80 mesh Carboxen 1000 and 60/80 mesh Carbosieve SIII were used for sample concentration. An Agilent 5890 series II gas chromatograph and an Agilent 5972 MSD were used for species identification and quantification. Volatile organic compounds were separated on a 60 meter, 0.32 mm I.D. fused silica capillary column with a 1.0 μm film thickness of J&W DB-1 bonded liquid phase.

Air from the canister was drawn through the LiOH packed tube and concentrated onto a sorbent. Sample volumes were measured with a mass flow controller at a fixed flow rate, 100 mL/min. Normally, 500 mL of stack sample was passed through a LiOH tube to remove acid and $CO_2$ from stack gas and then concentrated onto the sorbent tube. Ten mL of internal standard was loaded onto the sorbent tube at the same time. The sorbent tube was purged with 500 mL of UHP air to flush out $CO_2$ from the sorbent tube. The sorbent tube was loaded onto ACEM Model 900 thermal desorption system. An internal flow of helium purges the tube of residual water vapour and air prior to transfer of the collected analytes to a capillary packed trap for refocusing, then into a GC-MS equipped with wide-bore capillary column and mass spectrometer.

Optimum results were obtained by temperature programming the GC column. Column temperature was initially held for 3 min at $-60^{\circ}C$, then raised to $250^{\circ}C$ at a rate of $8^{\circ}C\ min^{-1}$. The GC-MSD was operated in the selected ion monitoring mode (SIM). Identification of target analytes by SIM is based on a combination of chromatographic retention time and relative abundance of selected monitored ions. Two or three characteristic ions were monitored for each of approximately 145 hydrocarbon compounds found in urban air samples. Since the MSD acquires data for only target ions, this detection technique is considered highly specific and sensitive.

An instrument calibration standard was made from gas standards prepared in the laboratory of Environment Canada from three multi-component liquid mixtures and gas mixture cylinders purchased from Scott Environmental Technology Inc. Quantification was based on five-point linear regression calibration curves.

# 6. RESULTS

## 6.1 General Sampling Data

The general sampling data for the test program is presented in Table 1. This table includes the average velocity, volumetric flow rate (referenced to 25°C and 101.3 kPa), average stack temperature and average moisture. Average oxygen and carbon dioxide levels were determined from the flue gas samples by the procedure described in Section 3.5. The traverse data for each run and summaries are presented in Appendix I. Operating temperatures for the dual primary and single secondary chambers are also included in Appendix I.

The sampling strategy was devised to collect the samples over different segments of the cycle. This approach provides a more realistic profile of the emissions during the incineration cycle. During the first two days, the SVOC sampling was commenced at the start of the cycle. The particulate/metals run followed with the sampling on the second day commencing about 1 hour later than the sample collected on the first day. On the third day, sampling started with the particulate/metals followed by the SVOC run. The sampling for each test day commenced 35, 23 and 15 minutes following ignition of the primary burners. One VOC canister was collected during each SVOC traverse. The sampling schedule is illustrated in Figure 7.

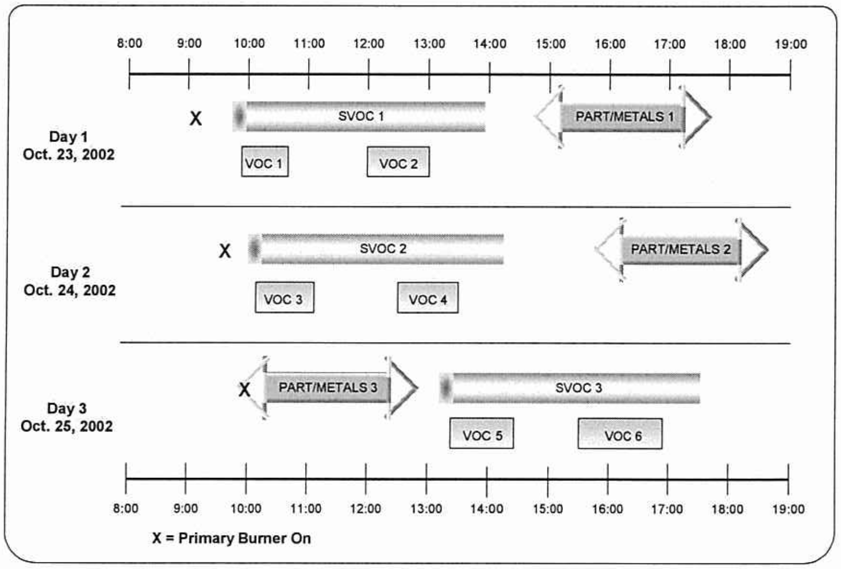


**Figure 7 Eco Waste Sampling Schedule**

The waste for the three days was delivered and piled outside the facility. Waste loaded to each primary chamber is recorded in Table 1. Two scenarios were used for the purpose of calculating emission rates – 100 and 250 cycles per year. These correspond to 2 and 5 cycles per week.

# Table 1 Summary of General Stack Sampling Data

| **Process Conditions** | | **Day 1** | | **Day 2** | | **Day 3** | |
|---|---|---|---|---|---|---|---|
| Date (Oct 2002) | | 23 | | 24 | | 25 | |
| Mass loaded (kg) | Primary 1 | 914 | | 909 | | 912 | |
| | Primary 2 | 916 | | 917 | | 917 | |
| Time Burners On | Secondary | 08:55 | | 09:25 | | 09:30 | |
| | Primary | 09:10 | | 09:38 | | 10:03 | |
| Primary Temperature (°C) | | See temperature profiles in Appendix I | | | | | |
| Secondary Temperature (°C) | | See temperature profiles in Appendix I | | | | | |
| **Sampling Conditions** | | **SVOC 1** | **Part/M-1** | **SVOC 2** | **Part/M-2** | **Part/M-3** | **SVOC 3** |
| Date (Oct 2002) | | 23 | 23 | 24 | 24 | 25 | 25 |
| Sampling Time (local) | | 09:45 - 13:53 | 15:07 – 17:15 | 10:01 - 14:10 | 16:07 – 18:11 | 10:18 – 12:24 | 13:16 – 17:26 |
| Test Duration (min) | | 240 | 120 | 240 | 120 | 120 | 240 |
| Isokineticity (%) | | 96.1 | 96.0 | 99.4 | 96.9 | 100.3 | 100.3 |
| Sample Volume ($m^3$) | | 4.075 | 1.891 | 3.894 | 1.903 | 1.983 | 4.043 |
| **Stack Gas Characteristics** | | | | | | | |
| Flow Rate ($m^3$/min) | | 71.64 | 66.79 | 65.73 | 66.72 | 67.04 | 67.74 |
| Actual Velocity (m/s) | | 6.78 | 5.90 | 5.98 | 5.88 | 6.25 | 6.13 |
| Temperature (°C) | | 705 | 666 | 669 | 671 | 688 | 675 |
| Moisture (%) | | 10.09 | 7.59 | 10.10 | 6.92 | 10.25 | 8.13 |
| Oxygen (%) | | 13.9 | 15.2 | 13.9 | 14.7 | 14.3 | 14.8 |
| Carbon Dioxide (%) | | 4.5 | 3.2 | 4.5 | 3.6 | 4.5 | 3.7 |
| Molecular Weight (lb/lb-mole) | | 29.28 | 29.12 | 29.28 | 29.16 | 29.29 | 29.18 |

*All volumes are expressed on a dry basis referenced to 25°C and 101.325 kPa.*

## 6.2 Particulate, Acid Gases and Metals

The concentrations of particulate, acid gases and metals are shown in Table 2. Particulate emissions ranged from 6 to 23 mg/m$^3$ (average 10.5 mg/m$^3$) corrected to 11 percent oxygen. The largest particulate level was observed in the third run where the sample was collected at the beginning of the burn cycle. Particulate levels for the two runs collected towards the end of the burn were 6.0 and 2.9 mg/m$^3$ with the latter value corresponding to the run collected closest to the end of the cycle. HCl levels ranged from 97 to 262 mg/m$^3$ with the higher value measured during the beginning of the burn. HF concentrations varied between 1.7 and 3.3 but the higher levels were measured towards the latter part of the batch cycle.

The front- and back-half fractions were analysed separately. As expected, all the mercury was associated with the back-half fraction. With the exception of three metals, the majority was consistently found in the front-half of the train. Two of these three metals, manganese and nickel, exhibited partitioning towards the front-half of the train in the run that was collected at the beginning of the cycle (77 and 84% respectively). The partitioning was skewed towards the back-half in the first and second runs for manganese (88/74%) and nickel (59/61%) respectively. In contrast, selenium distribution was skewed toward the back-half when the sample was collected at the start of the burn (70% in the back-half) compared to the two runs (71 and 66% in the front-half) collected towards the end of the cycle. Two metals, beryllium and thallium were not detected in the train samples. Mercury was detected in all runs but was very variable. Levels varied between 4.7 and 72.2 µg/m$^3$. For most of the metals, the levels in Run 3 (start of burn) were substantially higher than concentrations measured towards the end of the burn. No difference was noted for chromium.

The average (see note in Table 2) metal concentrations for the three runs are illustrated in Figure 8. Values are plotted on a logarithmic y-axis. Lead, copper, zinc and cadmium accounted for the majority of the reported metals (246, 214, 140 and 120 µg/m$^3$ respectively). Four metals, mercury, antimony, chromium and manganese, showed average concentrations between 10 and 100 µg/m$^3$. The remainder of the metals were below 10 µg/m$^3$ of which cobalt was below 1 µg/m$^3$. As mentioned previously, beryllium and thallium were not detected.

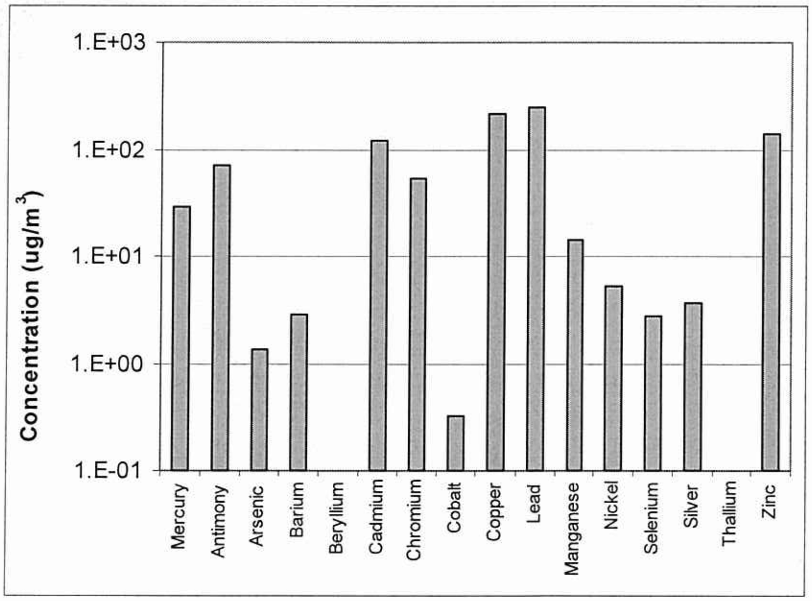


**Figure 8 Average Metal Concentrations (corrected to 11% oxygen)**

## Table 2 Summary of Particulate, Acid Gases and Metals Concentrations
(corrected to 11% oxygen)

| Pollutant | Part/M-1 | | Part/M-2 | | Part/M-3 | | Average* | |
|---|---|---|---|---|---|---|---|---|
| Particulate (mg/m$^3$) | 6.0 | | 2.9 | | 22.7 | | 10.5 | |
| HCl / HF (mg/m$^3$) | 97 | 3.3 | 113 | 4.0 | 262 | 1.7 | 157 | 3.0 |
| HCl / HF (ppm) | 65 | 4.0 | 76 | 4.9 | 175 | 2.0 | 105 | 3.6 |
| **Metals (µg/m$^3$)** | | | | | | | | |
| Mercury | 11.2 | | 72.2 | | 4.7 | | 29.4 | |
| Antimony | 32.6 | | 92.3 | | 90.8 | | 71.9 | |
| Arsenic | 0.9 | | 0.9 | | 2.2 | | 1.3 | |
| Barium | 0.2 | | 3.2 | | 5.3 | | 2.9 | |
| Beryllium | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Cadmium | 21.7 | | 35.4 | | 303 | | 120 | |
| Chromium | 56.5 | | 49.2 | | 53.4 | | 53.1 | |
| Cobalt | 0.3 | | 0.2 | | 0.5 | | 0.3 | |
| Copper | 138 | | 161 | | 343 | | 214 | |
| Lead | 62.1 | | 160 | | 515 | | 246 | |
| Manganese | 11.6 | | 10.4 | | 21.0 | | 14.4 | |
| Nickel | 2.9 | | 2.7 | | 10.2 | | 5.3 | |
| Selenium | 2.1 | | 2.7 | | 3.6 | | 2.8 | |
| Silver | 3.3 | | 3.5 | | 4.3 | | 3.7 | |
| Thallium | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Zinc | 57.7 | | 88.0 | | 274 | | 140 | |

*All volumes are expressed on a dry basis referenced to 25°C and 101.325 kPa.*
*"0" denotes not detected.*
** The average was based on the mean of the three runs.*

## 6.3 Flue Gases

The concentrations of oxygen, carbon dioxide, carbon monoxide, nitrogen oxides and sulphur dioxide are summarized in Table 3. Carbon monoxide, nitrogen oxides and sulphur dioxide are corrected to 11 percent oxygen. The values summarized in Table 3 represent the arithmetic average of the half-hour integrated bag samples. Detailed data for all the runs is given in Appendix I.

**Table 3 Summary of Flue Gas Concentrations**

| Run | $O_2$ (%) | $CO_2$ (%) | CO* (ppm) | NO* (ppm) | $NO_2$* (ppm) | $NO_x$* (ppm) | $SO_2$* (ppm) |
|---|---|---|---|---|---|---|---|
| **Part/M-1** | 15.2 | 3.2 | 9 | 50 | 4 | 54 | 0 |
| **Part/M-2** | 14.7 | 3.6 | 6 | 47 | 3 | 51 | 0 |
| **Part/M-3** | 14.3 | 4.5 | 4 | 45 | 4 | 49 | 0 |
| **SVOC 1** | 13.9 | 4.5 | 0 | 36 | 2 | 38 | 0 |
| **SVOC 2** | 13.9 | 4.5 | 3 | 40 | 3 | 43 | 2 |
| **SVOC 3** | 14.8 | 3.7 | 4 | 40 | 3 | 43 | 0 |
| **Ave**** | 14.4 | 4.1 | 3.6 | 41.7 | 3.0 | 44.7 | 0.5 |
| **Std Dev**** | 0.5 | 0.5 | 2.7 | 8.0 | 1.7 | 9.6 | 1.9 |

** Corrected to 11% oxygen. ** All data points*

In general, oxygen levels were 13.5 to 14 % at the start of the burn and increased to 15% by the end of the daily testing. Carbon dioxide followed the reverse trend, starting around 4.6 to 4.9% and decreasing to 3.1 to 3.5%. Sulphur dioxide was detected in only three of the integrated bag samples (SVOC 2). Carbon monoxide levels were below 10 ppm with only one bag sample slightly above 10 ppm. On average, NO represented 93% of the total $NO_x$. $NO_x$ levels showed a declining trend for the first four to five hours after the start of the daily sampling after which they increased for the remainder of the burn.

## 6.4 Dioxins and Furans

PCDD/PCDF data is reported on the basis of the seventeen 2,3,7,8-substituted dioxin and furan congeners. This data is further transformed by multiplying each of the 17 congeners by their respective toxicity equivalency factor (International-TEF or I-TEF). The factors range from 1.0 for 2,3,7,8- TCDD to 0.001 for OCDD and OCDF. The sum of all the 17 factored compounds is known as the TEQ. Analytical results of the loaded trains, field blank train, proofing and method blank samples are presented in Appendix II.

The emission summaries for the TEQ dioxins and furans are given in Table 4. The front- and back-half components of the SVOC train which correspond to the particulate and gaseous fractions respectively in the sample gas were combined for analysis. Train catches were corrected for the blank train. The blank train level was less than 0.35 pg TEQ/m$^3$.

The levels of the 17 congeners are shown in Figure 9. In all runs, the furan TEQ outweighed the dioxin TEQ. On a train total basis, the 10 furan compounds were very consistent representing 81 to 88% of the total train TEQ. Four furan congeners, 2,3,7,8-T4CDF, 2,3,4,7,8-P5CDF, 1,2,3,4,7,8-H6CDF and 2,3,4,6,7,8-H6CDF accounted for 67 to 71% of the total TEQ. On the TEQ basis, the 2,3,4,7,8-P5CDF congener was the largest component (26 to 30% of total) followed equally by 1,2,3,4,7,8-H6CDF (14 to 17%) and 2,3,4,6,7,8-H6CDF (14 to 18%). The 2,3,7,8-T4CDD congener was detected in all runs and accounted for 2.6 to 5.2% of the total TEQ. The congener profiles among the three runs are essentially identical.

Varying TEQ concentrations were measured during the testing. The highest level (71 pg TEQ/m$^3$) was measured in SVOC 3 which started about three hours after the ignition of the primary chambers. TEQ concentrations for the two tests conducted shortly after ignition were 10 and 36 pg TEQ/m$^3$. The simple average concentration was 38.9 pg TEQ/m$^3$. All concentrations are at 11% oxygen.

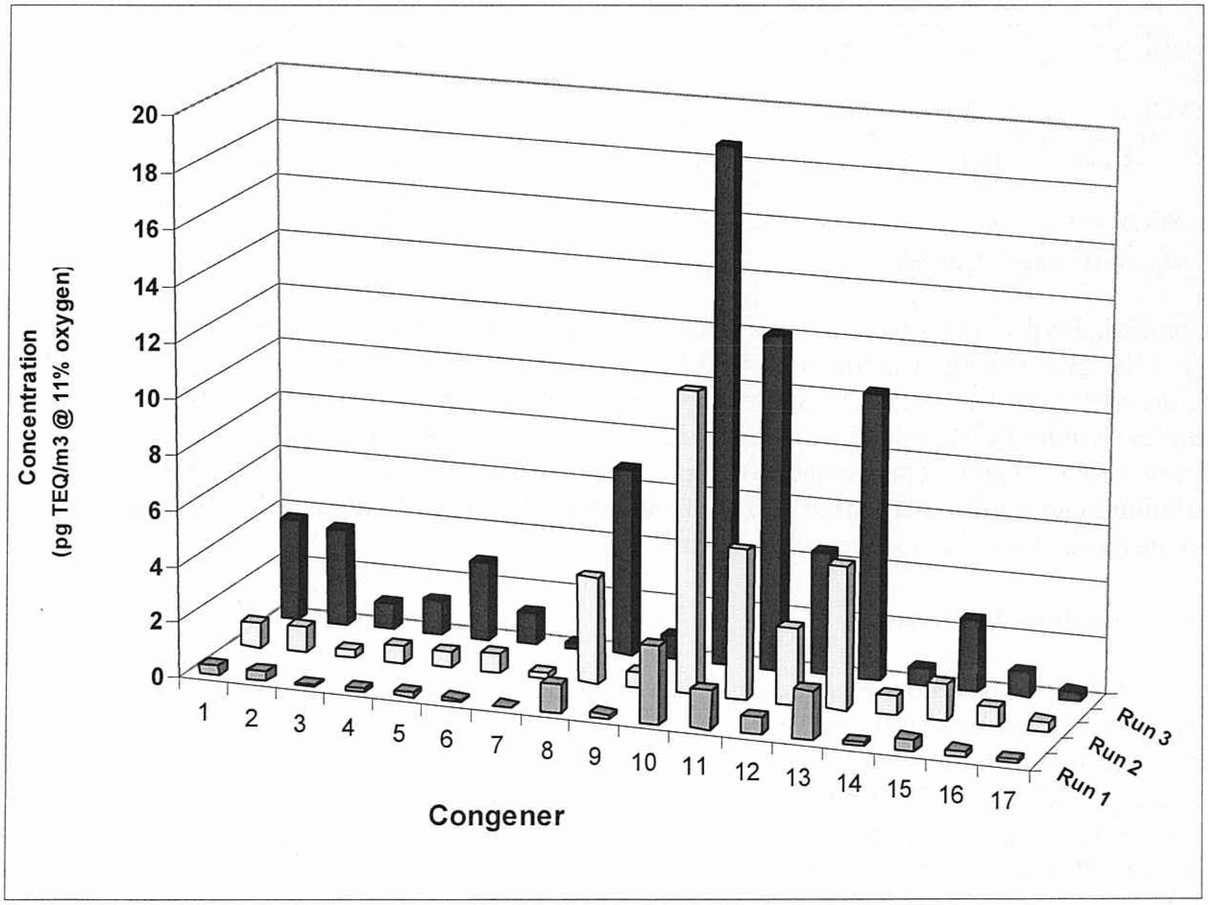


Figure 9 Distribution of TEQ Congeners

## Table 4 Concentrations of Dioxins and Furans
### (pg TEQ/m$^3$ @11% oxygen)

| Compound | SVOC 1 | SVOC 2 | SVOC 3 |
|---|---|---|---|
| 2378-T4CDD | 0.41 | 0.92 | 3.69 |
| 12378-P5CDD | 0.35 | 0.92 | 3.48 |
| 123478-H6CDD | 0.05 | 0.29 | 0.96 |
| 123678-H6CDD | 0.11 | 0.59 | 1.24 |
| 123789-H6CDD | 0.14 | 0.56 | 2.81 |
| 1234678-H7CDD | 0.12 | 0.71 | 1.17 |
| OCDD | 0.03 | 0.18 | 0.19 |
| 2378-T4CDF | 1.03 | 3.84 | 6.73 |
| 12378-P5CDF | 0.15 | 0.56 | 0.85 |
| 23478-P5CDF | 2.81 | 10.82 | 18.63 |
| 123478-H6CDF | 1.42 | 5.36 | 12.06 |
| 123678-H6CDF | 0.65 | 2.78 | 4.45 |
| 234678-H6CDF | 1.77 | 5.15 | 10.31 |
| 123789-H6CDF | 0.13 | 0.70 | 0.63 |
| 1234678-H7CDF | 0.44 | 1.30 | 2.56 |
| 1234789-H7CDF | 0.23 | 0.69 | 0.88 |
| OCDF | 0.13 | 0.37 | 0.33 |
| **TOTAL** | 9.98 | 35.73 | 70.98 |

*All values are expressed on a dry basis referenced to 25°C and 101.325 kPa.*
*Totals may not add due to rounding.*

## 6.5 Chlorobenzenes and Octachlorostyrene

The analysis of the SVOC train samples also included chlorobenzenes (CBs) and octachlorostyrene (OCS). Chlorobenzene compounds included 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene. Concentrations for the five selected chlorobenzenes and octachlorostyrene are summarized in Table 5 and Figure 10. Both train fractions were combined for the analysis of selected chlorobenzenes and octachlorostyrene. Pentachlorobenzene represented the largest component of the chlorobenzene isomers. Total selected CBs ranged between 3.4 and 44 ng/m$^3$. Similar to the TEQ dioxins and furans, the highest level for each of the detected compounds was measured in the run collected three hours after ignition. OCS was not detected in any of the three runs. Chlorobenzene concentrations are not corrected to 11 % oxygen.

**Table 5 Concentrations of Chlorobenzenes and Octachlorostyrene (ng/m$^3$)**

| Compound | SVOC 1 | SVOC 2 | SVOC 3 |
|---|---|---|---|
| **1,2,3,5-Tetrachlorobenzene** | 0.7 | 2.8 | 10.1 |
| **1,2,4,5-Tetrachlorobenzene** | 0.0 | 0.8 | 3.5 |
| **1,2,3,4-Tetrachlorobenzene** | 0.7 | 3.3 | 7.2 |
| **Pentachlorobenzene** | 1.2 | 3.6 | 17.3 |
| **Hexachlorobenzene** | 0.7 | 1.8 | 5.9 |
| **Total selected CBs** | 3.4 | 12.3 | 44.0 |
| **Octachlorostyrene** | 0.0 | 0.0 | 0.0 |

*Concentrations are expressed on a dry basis referenced to 25°C and 101.325 kPa.*
*"0" denotes not detectable.*

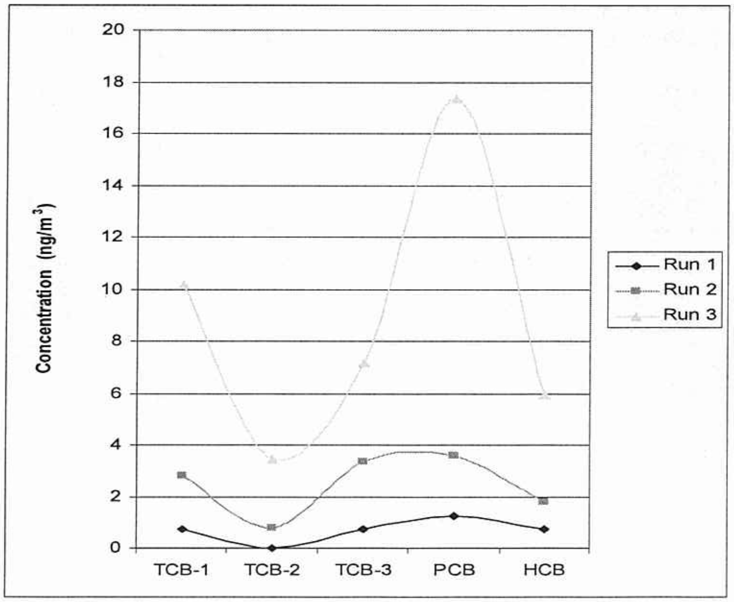


**Figure 10 Chlorobenzene Concentrations**

## 6.6 Polycyclic Aromatic Hydrocarbons (PAHs)

PAH concentrations are summarized in Table 6. As mentioned previously, the front- and back-halves of the sampling train were combined for analysis. Train catches were corrected for the PAHs detected in the blank train. Due to the low PAH loadings from this source, the PAH contribution from the blank, was substantial ranging from 44 to 66% of the uncorrected train catch. PAH analytical results of the loaded trains, blank train, proofing and control samples are presented in Appendix II.

Retene, a compound associated with wood combustion was added to the PAH list. The lighter half of the reported PAHs accounted for 82 to 99 % of the total. The heaviest PAH compound detected in at least one of the runs was benzo(g,h,i)perylene. Fluorene, phenanthrene, fluoranthene, pyrene and retene were the most abundant compounds accounting for 70 to 86% of all the reported PAHs for the three runs. Phenanthrene accounted for 33 to 42% of the total.

The totals for each train were low, ranging from 15 to 39 ng/m$^3$ (simple average 29 ng/m$^3$). These concentrations are not corrected to 11% oxygen. The highest levels were found in the runs that commenced sampling shortly after ignition of the primary. Little difference was noted between Run 1 and Run 2. A plot of the detected PAHs above 1 ng/m$^3$ is shown in Figure 11.

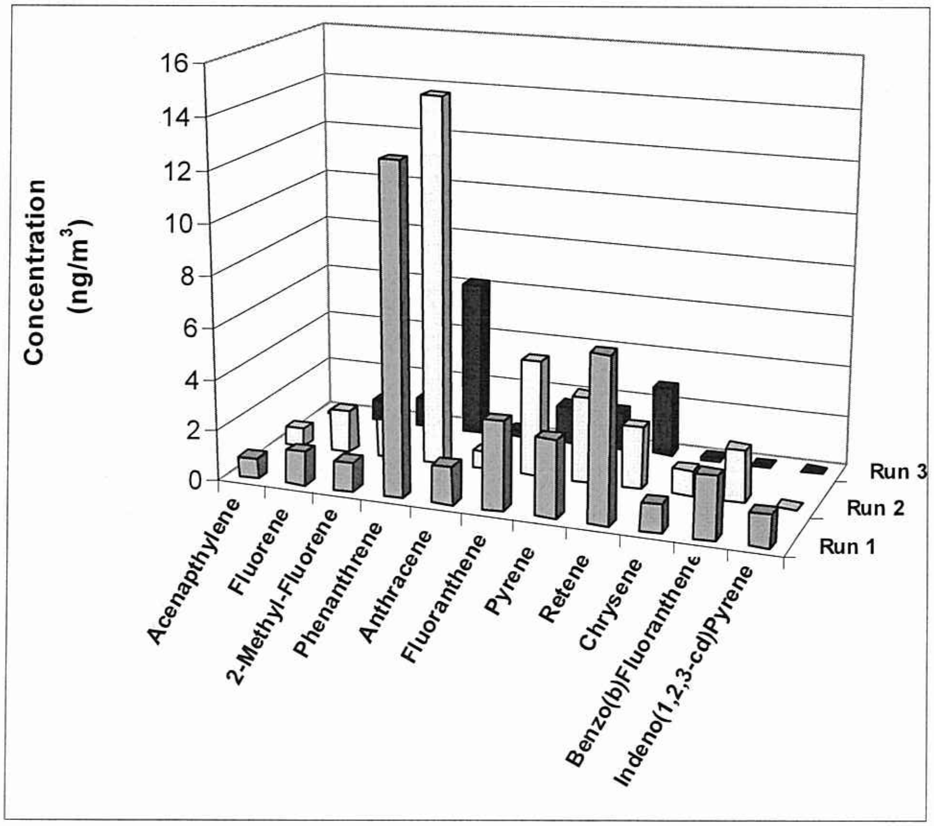


Figure 11 Selected PAH Concentrations

## Table 6 Concentrations of PAHs (ng/m$^3$)
### (corrected for blank train)

| Compound | SVOC 1 | SVOC 2 | SVOC 3 |
|---|---|---|---|
| Acenapthylene | 0.8 | 0.7 | 0.1 |
| Acenapthene | 0.0 | 0.0 | 0.2 |
| Fluorene | 1.3 | 1.7 | 0.8 |
| 2-Methyl-Fluorene | 1.2 | 1.5 | 1.1 |
| Phenanthrene | 12.8 | 14.5 | 6.1 |
| Anthracene | 1.5 | 0.7 | 0.2 |
| Fluoranthene | 3.5 | 4.6 | 1.5 |
| Pyrene | 3.0 | 3.4 | 1.5 |
| Retene | 6.5 | 2.4 | 2.7 |
| Benzo(a)Fluorene | 0.0 | 0.2 | 0.2 |
| Benzo(b)Fluorene | 0.0 | 0.0 | 0.0 |
| 1-Methyl-Pyrene | 0.0 | 0.2 | 0.1 |
| Benzo(g,h,i)Fluoranthene | 0.0 | 0.3 | 0.0 |
| Benzo(a)Anthracene | 0.5 | 0.4 | 0.0 |
| Triphenylene | 0.4 | 0.3 | 0.1 |
| Chrysene | 1.1 | 1.0 | 0.1 |
| 7-Methyl-Benzo(a)Anthracene | 0.0 | 0.0 | 0.0 |
| Benzo(b)Fluoranthene | 2.4 | 2.0 | 0.0 |
| Benzo(k)Fluoranthene | 0.5 | 0.0 | 0.0 |
| Benzo(e)Pyrene | 0.9 | 0.7 | 0.0 |
| Benzo(a)Pyrene | 0.0 | 0.0 | 0.0 |
| Perylene | 0.0 | 0.0 | 0.0 |
| 3-Methyl-Cholanthrene | 0.0 | 0.0 | 0.0 |
| Indeno(1,2,3-cd)Pyrene | 1.3 | 0.0 | 0.0 |
| Dibenzo(a,h)Anthracene | 0.0 | 0.0 | 0.0 |
| Benzo(b)Chrysene | 0.0 | 0.0 | 0.0 |
| Benzo(g,h,i)Perylene | 0.9 | 0.0 | 0.0 |
| Anthanthrene | 0.0 | 0.0 | 0.0 |
| ***TOTAL*** | 38.6 | 34.7 | 14.9 |

*Values expressed on a dry basis referenced to 25°C and 101.325 kPa.*
*"0" denotes not detectable.*

## 6.7 Volatile Organic Compounds (VOCs)

The full VOC target list contains 145 compounds, however this list was pared down for reporting purposes as many of the species are of lesser interest. Normally the list is reduced to include BTEX (benzene, ethylbenzene, toluene and xylenes) and halogenated hydrocarbons. Benzene and some halogenated hydrocarbons such as vinyl chloride, 1,3-butadiene, dichloromethane, tri and tetrachloroethene, carbon tetrachloride, 1,1,1-trichloroethane, 1,2-dichloroethane and hexachlorobutadiene are classified as CEPA-toxic substances. Naphthalene, a PAH compound, was also included since it is not reliably determined using the modified Method 5 type train. The full list of VOC concentrations is given in Appendix II.

The emission data for VOCs of interest is summarized in Table 7. Two canister samples were collected during each SVOC run. These are reported separately in Table 7.

**Table 7 Concentrations of Selected VOCs (μg/m$^3$)**

| Compound | SVOC 1 | | SVOC 2 | | SVOC 3 | | Overall Average |
|---|---|---|---|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 1 | Sample 2 | Sample 1 | Sample 2 | |
| Chloromethane | 0.79 | 4.56 | 1.34 | 2.31 | 1.57 | 0.85 | 1.90 |
| **Vinyl chloride** | 0.00 | 1.72 | 0.26 | 1.07 | 0.36 | 0.44 | 0.64 |
| **1,3 Butadiene** | 0.00 | 11.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.83 |
| **Dichloromethane** | 2.55 | 2.64 | 2.24 | 2.82 | 1.43 | 1.03 | 2.12 |
| **Benzene** | 1.79 | 99.80 | 1.60 | 1.43 | 1.87 | 0.95 | 17.91 |
| Toluene | 5831 | 2072 | 1258 | 2660 | 1170 | 713 | 2284 |
| Chlorobenzene | 0.10 | 3.72 | 0.12 | 0.26 | 0.09 | 0.07 | 0.73 |
| Ethylbenzene | 1.88 | 17.64 | 0.79 | 1.08 | 0.52 | 0.28 | 3.70 |
| Total Above | 5838 | 2213 | 1265 | 2668 | 1176 | 717 | 2313 |
| All reported VOCs | 5871 | 3213 | 1293 | 2695 | 1191 | 731 | 2499 |

*All values are expressed on a dry basis referenced to 25°C and 101.325 kPa.*
*Compounds denoted in bold are CEPA-toxic compounds.*

With the exception of sample 2 in SVOC 1, the VOCs reported in Table 7 accounted for +98% of the total VOCs. A high level of propene (verified by reanalysis) was measured in second sample of the first SVOC run. Three CEPA-toxic compounds, 1,2-dichloroethane and 1,1,1-trichloroethane and hexachlorobutadiene were analyzed for but not detected. Other toxics such as carbon tetrachloride, tri and tetra chloroethene were detected but at levels below those usually found in ambient air. Two of the naphthalene results showed levels slightly above ambient.

Toluene, normally found in combustion sources, was the most abundant compound accounting for practically all the detected volatile organic compounds. The higher toluene value in the first canister of the first SVOC run was confirmed by reanalyzing the canister. Except for the benzene, toluene and ethylbenzene reported above, other components of BTEX were detected but were found to be around those levels normally found in ambient air.

No agreement was evident among the three pairs of canisters. Using pair averages, the total VOCs for each of the three runs were 4540, 1994 and 960 μg/m$^3$. The average VOC level is in the order of 600 ppb on a volume/volume basis. The highest levels of VOCs were measured in the samples collected at the start of the cycle (SVOC1 and SVOC 2). No pattern was evident between the first and second canister of each SVOC run.

## 6.8 Estimated Emission Rates

The annual emission rates for the particulate/metals and organic runs are given in Table 9. One of the difficulties associated with the calculation of the emission rates is the estimation of the concentration over the oxidizer cycle for each of the pollutants. Pollutant levels are a result of feed material, process operation and the portion of the burn cycle in a batch process. In this program, sampling was staggered as much as possible to provide a more representative variation of the emissions over the cycle.

Normally, the concentration used for calculating emission rates is the arithmetic average of three runs. In this case, this approach may introduce a bias for some of the pollutants as two of the runs were essentially duplicates of the same portion of the cycle. A selective average was also calculated based on the average between the two runs collected during the same part of the cycle and the remaining run. A comparison of these two averaging techniques is illustrated in Table 8.

**Table 8 Effect of Averaging Method on Uncorrected Concentrations**

| Pollutant | Three Run Average | | Selective Average | |
|---|---|---|---|---|
| **Particulate/Acid Gases/Metals** | | | | |
| Particulate (mg/m$^3$) | 6.78 | | 8.87 | |
| HCl / HF (mg/m$^3$) | 100.3 | 1.8 | 118.9 | 1.6 |
| Mercury | 18.27 | | 14.49 | |
| Antimony | 45.70 | | 49.40 | |
| Arsenic | 0.86 | | 1.01 | |
| Barium | 1.89 | | 2.30 | |
| Cadmium | 78.9 | | 109.7 | |
| Chromium | 33.00 | | 33.66 | |
| Cobalt | 0.20 | | 0.23 | |
| Copper | 136.4 | | 159.5 | |
| Lead | 159.7 | | 205.6 | |
| Manganese | 9.09 | | 10.32 | |
| Nickel | 3.39 | | 4.23 | |
| Selenium | 1.75 | | 1.90 | |
| Silver | 2.33 | | 2.46 | |
| Zinc | 90.3 | | 113.3 | |
| **Organics** | | | | |
| Dioxins and Furans (pg TEQ/m$^3$) | 25.35 | | 29.95 | |
| PAHs (ng/m$^3$) | 29.40 | | 25.78 | |
| CBs (ng/m$^3$) | 19.93 | | 25.95 | |
| VOCs (µg/m$^3$) | 2499 | | 2115 | |

Table 8 shows that the selective approach results in higher average concentrations for particulate, HCl, most metals, dioxins and furans and chlorobenzenes. VOCs and PAHs display the opposite bias. The difference for mercury is irrelevant as the emissions are probably directly related to the feed input. Neither method is invalid but this exercise serves to illustrate that the assumptions have an impact on emission levels. For the purpose of this program, the simple average of three runs will be used to estimate annual emissions. Two scenarios were used for estimating annual emission rates – 100 and 250 cycles per year.

### Table 9 Estimated Annual Emission Rates

**BASIS: AVERAGE OF THREE RUNS**
**Ten hour cycle**
**100 and 250 batches per year**
**Stack flow rate - average of all runs**

| **Pollutant** | **Average* Concentration** | **Annual Emission Rate** | |
|---|---|---|---|
| | | **100 batches** | **250 batches** |
| **Particulate, Acid Gases and Metals** | | | |
| Particulate | 6.78 mg/m$^3$ | 27.5 kg/year | 68.8 kg/year |
| HCl | 100.2 mg/m$^3$ | 407 kg/year | 1017 kg/year |
| HF | 1.83 mg/m$^3$ | 7.4 kg/year | 18.5 kg/year |
| | (µg/m$^3$) | (g/year) | (g/year) |
| **Metals** | | | |
| Mercury | 18.3 | 74 | 185 |
| Antimony | 45.7 | 185 | 463 |
| Arsenic | 0.9 | 3 | 9 |
| Barium | 1.9 | 8 | 19 |
| Beryllium | not detected | - | - |
| Cadmium | 78.9 | 320 | 800 |
| Chromium | 33.0 | 134 | 335 |
| Cobalt | 0.2 | 1 | 2 |
| Copper | 136.4 | 553 | 1384 |
| Lead | 159.7 | 648 | 1619 |
| Manganese | 9.1 | 37 | 92 |
| Nickel | 3.4 | 14 | 34 |
| Selenium | 1.7 | 7 | 18 |
| Silver | 2.3 | 9 | 24 |
| Thallium | not detected | - | - |
| Zinc | 90.3 | 366 | 916 |
| **Organics** | | | |
| Dioxins and Furans (TEQ) | 25.35 pg TEQ/m$^3$ | 0.103 mg/year | 0.257 mg/year |
| TCB (3 isomers) | 9.73 ng/m$^3$ | 0.039 g/year | 0.099 g/year |
| PCB | 7.38 ng/m$^3$ | 0.030 g/year | 0.075 g/year |
| HCB | 2.82 ng/m$^3$ | 0.011 g/year | 0.029 g/year |
| PAHs | 29.4 ng/m$^3$ | 0.119 g/year | 0.298 g/year |
| OCS | not detected | - | - |
| VOCs | 2499 µg/m$^3$ | 10.1 kg/year | 25.3 kg/year |

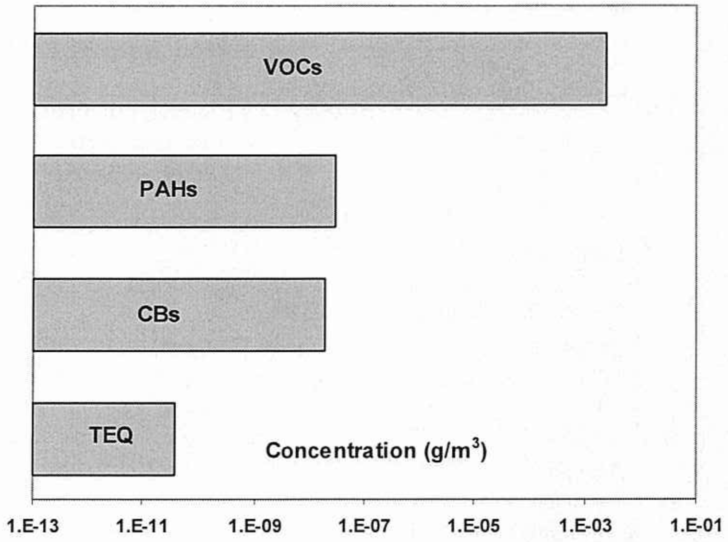
* *Uncorrected concentrations at reference conditions used to calculate emission rates.*

## 7. SUMMARY

Concentration data is summarized below. The relative abundances (on a logarithmic scale) for the organic compounds and metals are illustrated in Figure 12.

| Compound | Concentration |
|---|---|
| PCDDs/PCDFs* | 38.9 pg TEQ/m$^3$ |
| CBs (5 isomers) | 19.9 ng/m$^3$ |
| OCS | 0 ng/m$^3$ |
| PAHs | 29.4 ng/m$^3$ |
| VOCs | 2499 µg/m$^3$ |
| Particulate* | 10.5 mg/m$^3$ |
| HCl* | 157 mg/m$^3$ |
| HF* | 3.0 mg/m$^3$ |

** at 11% oxygen*
*0 denotes not detected.*



| Metals* (µg/m$^3$) | |
|---|---|
| Mercury | 29.38 |
| Antimony | 71.9 |
| Arsenic | 1.3 |
| Barium | 2.9 |
| Beryllium | 0.0 |
| Cadmium | 120.0 |
| Chromium | 53.1 |
| Cobalt | 0.3 |
| Copper | 214.2 |
| Lead | 245.5 |
| Manganese | 14.4 |
| Nickel | 5.3 |
| Selenium | 2.8 |
| Silver | 3.7 |
| Thallium | 0.0 |
| Zinc | 139.8 |

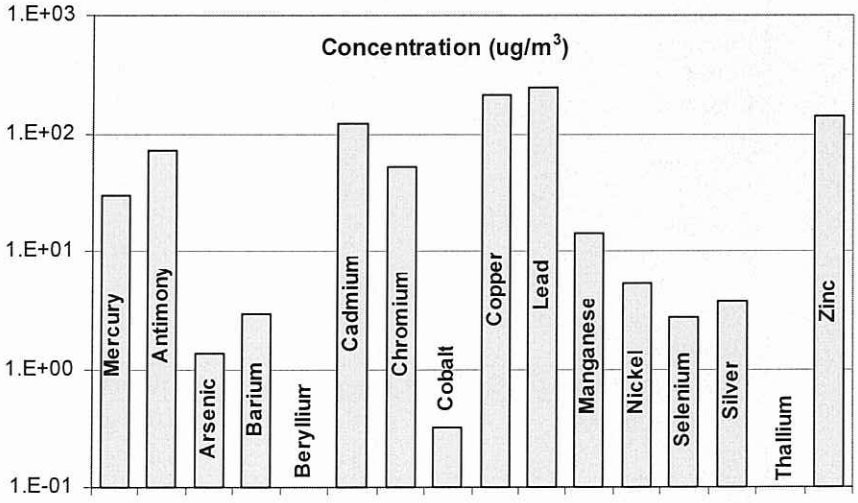


**Figure 12 Summary of Emission Results**

# APPENDIX I

(Only available with hard copy)

## Waste Oxidizer Temperature Data

## Flue Gas Monitoring Data

## SVOC Traverse Data

## Particulate /Metals Traverse Data

# APPENDIX II

(Only available with hard copy)

## Anion, Particulate and Metals Analysis

## Dioxin, Furan, CB and OCS Analytical Report

## VOC Analytical Data