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**COLE DRAIN (SARNIA) CONTAMINANT
CONCENTRATIONS AND LOADINGS - 1995**

April, 1999

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**COLE DRAIN (SARNIA) CONTAMINANT
CONCENTRATIONS AND LOADINGS - 1995**

by

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April, 1999

EXECUTIVE SUMMARY

Analysis of bottom sediment and suspended sediment samples collected in the upper St. Clair River during 1994 revealed substantial increases in the concentrations of mercury and certain chlorinated aliphatic and aromatic compounds between the upstream control samples obtained near the Esso intake and those from downstream of the Bayer outfalls and the Dow 2nd Street sewer. It was felt that the presence of these persistent, bioaccumulative contaminants in the river could be due to ongoing inputs from existing point source discharges such as the Cole Drain, and/or resuspension of historically contaminated sediments. The latter possibility was investigated by the Ministry as part of the sediment fate and transport modelling initiative.

Therefore, in 1995, effluent samples were collected from the final mixing chamber of the Cole Drain in Sarnia to determine the concentrations and the loadings of contaminants from this source to the river. The samples included both whole-water (i.e., aqueous plus particulate fractions) as well as suspended sediment (i.e., particulate fraction only) samples. OMOE Environmental Monitoring and Reporting Branch staff sampled the effluent during surveys in June and August - each of three to four days' duration. The whole-water samples were each analyzed for 88 parameters or contaminants, and the particulates for 136. In addition, whole-water samples were collected in late November by Ministry Sarnia District Office staff at several locations within the Cole Drain and Scott Road Ditch system. Coincident with the latter sampling, water samples were collected in the river by diver, both upstream and downstream of the outfall diffuser.

Contaminants Concentrations

The more routine or "conventional" parameters monitored, including calcium, chloride, magnesium, nitrogen, phosphorus, dissolved inorganic and organic carbon, suspended solids, as well as many of the heavy metals, were detected at parts per million to parts per billion levels in all of the whole-water effluent samples. Also, certain chlorinated aliphatics and aromatic contaminants, known to be chemical intermediates or waste by-products of chlorinated solvents manufacturing, were also consistently found in the effluent at parts per trillion levels. These included: hexachlorobuta-diene (HCBD), pentachlorobenzene (PentaCB), hexachlorobenzene (HCB) and octachlorostyrene (OCS).

The collection and analysis of effluent particulates by centrifugation considerably enhanced both the detection and the quantification of contaminants present at low levels in the discharge. Consequently, besides the "conventional" parameters, additional inorganics and heavy metals, many chlorinated aliphatics and aromatics, and polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were found in effluent particulates. Although not detected (i.e., not present above the minimum reportable value of the analytical method) in the effluent whole-water samples, PCBs and most of the polycyclic aromatic hydrocarbon (PAH) compounds were

present in the particulate fraction. Of the PAHs, phenanthrene, fluoranthene and pyrene concentrations were the highest. Octachlorinated isomers dominated the concentration profile of PCDDs and PCDFs in the particulates.

Higher mean whole-water effluent and/or particulate-associated concentrations in the Cole Drain discharge than in lower Lake Huron water sampled at Point Edward indicate that the discharge is a potentially important source to the St. Clair River of (at least) the following contaminants: chloride, dissolved organic carbon total Kjeldahl nitrogen, total phosphorus, aluminum, cobalt, copper, iron, manganese, molybdenum, nickel, vanadium, zinc, hexachloroethane, HCB, 1,2,4,-trichlorobenzene (TriCB), 1,3,5-TriCB, PentaCB, HCB, OCS, fluoranthene, phenanthrene, pyrene, and Total PCBs. Of these parameters, chloride, total Kjeldahl nitrogen, total phosphorus, copper, manganese, nickel, zinc, HCB, HCB, OCS and (as a group) PAHs are on the St. Clair River Remedial Action Plan “Contaminants of Concern” list. Also included on this list are the PCDDs and PCDFs, representatives of which were detected in all of the effluent particulates samples. This list includes those contaminants which have exceeded Ontario, Michigan or Great Lakes Water Quality Agreement objectives or standards for water, sediment or aquatic biota. It was compiled during the St. Clair River RAP Stage 1 process to assist in: determining the potential impact from existing sources and assessing the need for additional remediation; and, measuring progress towards the virtual elimination of persistent toxic substances within the Great Lakes Water Quality Agreement philosophy of zero discharge (adopted by the RAP during the Stage 2 process).

Contaminants Loadings

Of the parameters measured, estimated average daily loadings of the “conventionals” were the largest. In order of decreasing magnitude, these included: calcium, chloride and dissolved inorganic carbon, ranging from 4.7 to 2.3 tonnes per day; organic carbon, magnesium, suspended solids and solvent extractables, at 850 to 130 kilograms per day; and nutrients, including nitrogen, phosphorus and silicon, ranging from 60 to 7.5 kg.d⁻¹.

Metals and chlorinated organic contaminants contributed a much smaller daily loading to the St. Clair River. Of these two groups, inorganic and heavy metal inputs were the greatest. The highest loadings were of aluminum and strontium (from 19.0 to 10.5 kg.d⁻¹), followed by iron and barium (6.6 to 1.4 kg.day⁻¹), then by manganese, zinc, nickel, copper, cobalt, molybdenum, vanadium, chromium, titanium, lead (2.6 to 0.019 kg.d⁻¹), and lastly by arsenic, cadmium and mercury (3 to 0.05 grams per day).

Daily loadings of organic contaminants were generally in the range of 0.24 to 30 grams per day. The greatest loadings were of the chlorinated organics HCB, OCS and HCB. Particulate-associated loadings of total PCBs and of individual PAH compounds were generally one to two orders of magnitude lower than for these chlorinated organics, ranging from 0.009 to 0.125 g.d⁻¹. As indicated previously however, PCBs and PAHs were not found in any whole-water effluent samples, and therefore, these particulate-derived loadings should be considered as minimal

values in the overall effluent loadings evaluation. Particulate-associated loadings of PCDDs and PCDFs were three orders of magnitude lower than for the other trace organics: total PCDD plus total PCDF (PCDD/F) homolog inputs ranged from 0.580 to 0.787 milligrams per day. The total loading of toxic isomers, i.e., the Total 2,3,7,8-TetraCDD Toxic Equivalence, was from 0.004 to 0.010 mg.d⁻¹, or 0.6 to 1.3% of the total PCDD/F homolog loading. A number of these organic contaminants, including HCB, HCB, OCS, PCBs, PAHs, PCDDs and PCDFs are persistent and bioaccumulative in the aquatic ecosystem.

The potential variability of contaminants loadings was estimated using the minima and maxima of the survey contaminant concentrations and of historical flow data. This indicated that depending on the matrix (unfiltered effluent vs. particulate) and the specific contaminant, the minimum and maximum loadings could differ by as little as two-fold to as much as 20-fold or more. This may be related mainly to the high short-term variation in the concentration of certain contaminants.

The relative contribution of particulate-associated contaminants to the total loading of contaminants from the Cole Drain effluent was parameter-dependant. Most of the “conventional” parameters were in the aqueous phase, the particulate-associated loading contributed 20 % or less of the total effluent loading. Only the particulate-associated loadings of aluminum, chromium, copper, iron and zinc constituted more than 20 % or more of the total loading, with those for aluminum, chromium and iron ranging from 75 to 100 %. Chlorinated organic compounds such as HCB and OCS, with high organic carbon partition coefficients (and therefore expected to be found mainly in the particulate phase), contributed a surprisingly small proportion of the total loading via particulates (i.e., as much as 86 % for OCS in the August survey, but usually under 35 %), particularly during the June survey. The fact that a major proportion of the loadings of some of these compounds was mainly aqueous and not particulate-associated suggests that they may be more readily available for accumulation by resident aquatic biota immediately after their discharge to the river.

Importance of Cole Drain Loadings

For many of the non-organic contaminants identified in the final effluent, the Cole Drain input seems to constitute only a small fraction (i.e., from 0.005 % for iron or lead, to 3.4 % for magnesium) of the total inputs added by all sources to the St. Clair River between Lake Huron and Lake St. Clair.

Comparison of the average 1995 loadings data with mid-1980s information suggests that Cole Drain inputs of certain contaminants may be decreasing over time. The latter include chloride, total Kjeldahl nitrogen, oil and grease, suspended solids, aluminum, copper, iron, molybdenum, zinc, phenolics, HCE, HCB, HCB, 1,2,4,-TriCB and 1,3,5-TriCB. For example, the mean HCE and HCB loadings in 1995 were below their St. Clair River MISA Pilot Site Study-recommended load allocations, which were set to provide compliance with water quality objectives 95 % of the time. A decreasing trend was also noted for the concentrations of some contaminants measured

by the long-term, year-round head and mouth monitoring of the St. Clair River by Environment Canada. For example, there were significant decreases between 1988 and 1989 in the concentrations of 1,3,5-TriCB, HCB, PentaCB, HCB and OCS in suspended sediment samples collected in the lower river at Port Lambton. Over the period 1990 to 1995, there was a large decrease in the aqueous phase (i.e., particulates removed) chloride concentration at Port Lambton. Similarly, the aqueous phase HCB concentration and particulate-associated concentrations of 1,3,5-TriCB, HCB, PentaCB, HCB and OCS at Port Lambton exhibited a steady decline since 1988, although their levels are still noticeably higher in summer samples. The largest decreases in most of these contaminants occurred during the 1988-1991 period, with concentrations having levelled off since then.

As of 1995, the Cole Drain continued to be an important point source of a number of the organic contaminants to the river (i.e., on average, from 3% to 72 % of the difference between Lake Huron input and lower river output loadings), particularly the more persistent and bioaccumulative chlorinated aliphatic and aromatic compounds, which include HCB, PentaCB, HCB and OCS. The average 1995 Cole Drain loadings of HCB and OCS were 1.5 and 920 times greater than the recommended load allocations proposed from receiving water-based modelling of the extensive data obtained during the 1986 St. Clair River MISA Pilot Site Organic Chemicals Sector Study. The June and August 1995 effluent samples exceeded the Provincial Water Quality Objectives and/or RAP Yardsticks for phosphorus, aluminum, cobalt, HCB and HCB in a majority of the samples from both surveys, usually by about two-fold, and up to 100-fold for HCB and 760-fold for HCB. Samples collected in November, 1995 in the final effluent exceeded the Provincial Water Quality Objectives for the Protection of Aquatic Life by factors of 61 for HCB, 1.5 for PentaCB and 2.3 for HCB. They also exceeded the St. Clair River Environmental Water Quality "Yardsticks" by factors ranging from 5.5 for HCB to 15 for HCB. (The Yardsticks were derived from a review of criteria from the five concerned jurisdictions. They represent the lowest, scientifically valid criterion available for each contaminant and were proposed as the concentrations to be achieved as a result of remedial measures.) Within the discharge plume in the St. Clair River and somewhat further downstream, the PWQOs were exceeded by factors of 44 and 15 for HCB, 1.3 for PentaCB, and 4.6 and 1.1 for HCB. Although OCS was also present, no objective or guideline is currently available for this compound.

Potential Sources of Contaminants to the Cole Drain

The presence of chlorinated aliphatics and aromatics (dominated by HCB) - as well as PAHs, PCBs, PCDDs and PCDFs - in the Cole Drain final effluent suggests that as of 1995, there were ongoing contaminant inputs or sources within the Cole Drain system. These may include losses from landfills. A number of the above chlorinated contaminants were disposed of in landfills bordering the Cole Drain-Scott Road Ditch system, e.g., the Dow Chemical Scott Road landfill. The detection of high concentrations of chlorinated aliphatics and aromatics in the Polysar Flyash Pond Drain and the Scott Road Drain (which contains leachate from the Dow Scott Road landfill) effluents, coupled with the similarity of the Scott Road Drain effluent and the Cole

Drain discharge contaminant profiles (again, with HCBd dominating), suggests that these two contributing discharges, particularly the Scott Road Drain, are important sources of these organic compounds. Additionally, the similarity of the Cole Drain sediment to the final effluent contaminant profile suggests that the resuspension or erosion of contaminated sediments and/or soils within the system may also constitute a source of these contaminants to the discharge.

Report Audience and Use of the Study Results

This report is being provided to the St. Clair River Remedial Action Plan Team and Binational Public Advisory Committee, the Southwestern Region and Sarnia District Offices, and to the Lambton Industrial Society to assist in identifying remaining contaminants sources requiring remedial measures.

Subsequent to and partially as a result of data from this study and from samples collected by Sarnia District Office staff, substantial work was undertaken by Dow Chemical Canada Inc., Bay Inc. and Owens-Corning Canada Inc. at the respective landfill sites in the Scott Road area. This work is on-going and will probably not be completed until mid-1999. For example, Dow committed to eliminate all chlorinated contaminant discharges/leachate to the Cole Drain (Geomatics, 1997) and in 1997 initiated a program to identify and contain contaminants leaching from its Scott Road landfill. This included: the installation of an additional interlocking sheet pile barrier wall around the landfill; the separation of stormwater from contaminated groundwater by the installation of a new municipal sewer and disconnecting the Scott Road sewer from the Cole Drain; and the removal of the contaminated sewer pipe and associated soil (G. Sober, OME, pers. comm., 1997). Also, on February 16, 1998, Environmental Protection Act loading limits for contaminants permitted to be discharged into the Cole Drain by the Scott Road Landfill wastewater treatment system came into force. Since the Dow Scott Road Landfill has been a major source of a number of contaminants to the Cole Drain - particularly the chlorinated aliphatics and aromatics - these new limits (if achieved) should assist greatly in reducing contaminants inputs to the St. Clair River. Consequently, Cole Drain contaminants concentration and loading data from this report should be compared to future effluent samples to assess the efficacy of the above and other remedial measures undertaken within the Cole Drain system.

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1.0 INTRODUCTION

During 1994 and 1995, the Ontario Ministry of the Environment conducted a Sediment Impact Zone Characterization study in the upper St. Clair River. This revealed a pronounced increase in the concentrations of certain contaminants in nearshore surficial sediments downstream of the Cole Drain discharge. For example, the maximum sediment mercury concentration at the south end of the Bayer (previously Polysar) Rubber property was nine-fold higher than just upstream of the Cole Drain outfall (see Fig. 1 for locations). Similarly, hexachlorobutadiene (HCBD) increased by over 35-fold; hexachlorobenzene (HCB) by over 20-fold; and octachlorostyrene (OCS) by more than 800-fold over the same distance (Kauss, 1999). These organic contaminants were identified as early as the late 1970s in some Sarnia industrial discharges and environmental samples (e.g., Duholke & Meresz, 1977; Bonner & Meresz, 1981).

Sediment traps were also installed by the Ministry in the nearshore of this study area: transect 18 near the Esso intake (the furthest upstream); transect 22 at the bottom end of Bayer Rubber; and transect IS 15, just downstream of the Dow Chemical 2nd Street sewer discharge (see Fig. 1). A large quantity of fine sediment was collected in these traps during their four month exposure period in 1994. Chemical analysis revealed substantial increases in the concentrations of mercury and certain chlorinated aliphatic and aromatic compounds between the upstream control samples obtained near the Esso intake and those from downstream of the Bayer outfalls and the Dow 2nd Street sewer (Kauss, 1999). A similar trend was observed in sediment trap samples collected during two periods in 1995 (*ibid*). It was felt that the presence of these persistent, bioaccumulative contaminants in sediments and suspended sediments along the Bayer-Dow nearshore may be the result of ongoing inputs from existing point source discharges such as the Cole Drain, and/or resuspension of historically contaminated sediments. The latter possibility was investigated by the Ministry as part of the sediment fate and transport modelling initiative (Tomczak, 1996; Haralampides *et al.*, 1997; McCorquodale & Tomczak, 1998).

The Cole Drain (also called the Township Ditch, Municipal Ditch or Cutoff Drain) is about 8 km in length. It is mainly an open ditch system, with only the last 370 metres passing through twin underground sewers to the final mixing chamber located near the St. Clair River shoreline. In 1982, the shore-based discharge of the Cole Drain was extended 68 m offshore via a submerged 30 cm diameter pipe equipped with a diffuser (T. Erme, OMOE, pers. comm., 1997). The Cole Drain conveys surface runoff from an area of approximately 16 km² located upstream of Vidal Street (Marsalek, 1986) and south of Sarnia's residential and business core. It also receives industrial process effluent, cooling water and treated and untreated runoff from numerous facilities, as well as stormwater runoff from undeveloped and developed land, product storage areas and waste disposal sites (St. Clair River RAP Team, 1991). Present industrial dischargers to the drain include: AMOCO Canada Petroleum Co. Ltd., Bayer Rubber and Cabot Carbon. Storm water from the Canadian National Railways, City of Sarnia sewage sludge lagoon area, Imperial Oil Chemicals plant site, the former Owens Corning plant site, Nova Sarnia plant site and Bayer Rubber plant site (formerly BASF Canada Inc. and AKZO Chemicals Ltd.) also enters the drain. The Scott Road Ditch, a 1.5 km long tributary of the Cole Drain (Fig. 2), receives

Figure 1. Location of Cole Drain outfall (labelled number 4) relative to 1994/95 St. Clair River nearshore sediment and sediment trap sampling locations. Adapted from Farara & Burt (1997).

treated leachate and storm water from the Dow Chemical landfill site, storm water runoff from the Bayer, Owens Corning (formerly Fiberglas Canada Ltd.) and Imperial Oil landfill sites, and storm water from the Fibrex (formerly Partek) plant site, before combining with the upper part of the Cole Drain (St. Clair River RAP Team, 1991; T. Erme, OMOE, pers. comm., 1997).

Industrial wastes, including chlorinated tars, were disposed of in the Dow Chemical landfill, adjacent to Scott Road. In 1972, Dow installed an interlocking sheet steel dike, anchored in the underlying clay, around the landfill. In the same year, the company cleaned and replaced a concrete sewer pipe. Site surface water and leachate treatment with activated carbon began in 1978 (G. Szober, OMOE, pers. comm., 1997). This treated liquid is periodically discharged to the Scott Road Ditch (King & Sherbin, 1986). However, prior to the installation of the carbon filters, leachate from the Dow disposal site had already contaminated the Scott Road Ditch and Cole Drain sediments with chlorinated organic contaminants such as HCB and HCBd (OMOE, unpublished 1980 and 1981 data - see Appendix D). In 1982, the Scott Road Ditch section was excavated and replaced with a submerged sewer. During the 1983-1984 period, a 3.7 km long section of the Cole Drain as far as the Bayer (Polysar) property line was dredged by Dow, and the contaminated material placed in the Dow Scott Road landfill (EC & OMOE, 1986).

Results of the joint federal-provincial study in 1985 revealed that the Cole Drain effluent was a greater source of HCBd and trichlorobenzenes to the St. Clair River than the Dow 1st Street sewer complex. The study report recommended that "The effectiveness of the Dow Scott Road landfill carbon treatment facility be investigated." and that "Modifications should be implemented to reduce losses of persistent chlorinated organics, especially hexachlorobenzene and hexachlorobutadiene" (EC & OMOE, 1986). Additionally, the Upper Great Lakes Connecting Channels Study of 1984/85 identified the Cole Drain as the principal contributor of PAHs, oil and grease and cyanide to the St. Clair River (UGLCCS, 1989). Finally, for the 1986 through 1989 period, the Cole Drain discharge was identified as the primary source of oil and grease, total PAHs and octachlorostyrene to the river, as well as a secondary contributor of suspended solids, copper, cadmium, cyanide and hexachlorobenzene (St. Clair River RAP Team, 1991; Geomatics, 1993).

2.0 OBJECTIVES

This study was designed to determine:

- (i) the concentrations of persistent inorganic and organic as well as conventional contaminants in the Cole Drain final effluent; and
- (ii) the loadings of these contaminants to the St. Clair River.

Figure 2. Cole Drain and Scott Road Ditch sampling locations in 1995. Numbers relate to locations in Table 7.

3.0 FIELD METHODS

Sampling took place in the final effluent mixing chamber of the Cole Drain, located about 10 metres from the St. Clair River, just south of the north property line of Bayer Rubber (see Figs. 1 and 2). Sampling occurred during two three-day surveys, June 20-22 and August 21-24.

3.1 Collection of Particulates Samples

Time-composited samples of particulate matter (suspended sediment) were collected from the Cole Drain discharge using a March Model MAB5CMD submersible pump connected to two Alfa-Laval Model 103B continuous-flow centrifuges by a Teflon®-lined hose and flow splitter. The stainless steel bowl and plates of the centrifuge as well as the pump/tubing system were solvent (glass-distilled hexane)- and distilled water-rinsed between samples. The feed water flow rate to the centrifuge was maintained at a constant 6 litres.min⁻¹. Centrifugation can provide up to 90 % recovery of particles greater than 0.6 µm diameter (Chan, 1993). However, recovery efficiency is also related to density. Therefore, if a contaminant is to a large degree associated with dissolved organic matter, it will not be removed efficiently by centrifugation (Evers & Smedes, 1995).

Particulates samples were transferred directly to amber (trace organics grade) glass jars using a solvent-rinsed stainless steel spoon and stored at -15°C for about three months. The samples were then sub-divided among the required sample jars (OMOE, 1989a and updates) and submitted for analysis.

3.2 Collection of Whole-Water Samples

Discrete whole-water (unfiltered) effluent samples were obtained at approximately 3 hr intervals (during daylight hours only) from the influent flow to the centrifuges. Samples were collected directly in the appropriate sample bottles, preserved as required (OMOE, 1989a and updates), and immediately submitted for analysis.

Additional whole-water samples were collected during November 22-23 by OMOE Sarnia District Office staff at a number of locations within the Cole Drain and Scott Road Ditch system (Fig. 2), as well as in the final mixing chamber. Coincident with this sampling, water samples were collected by diver at three locations near the river bottom: just upstream of the Cole Drain outfall diffuser (located about 68 metres offshore); within the discharge plume (as delineated by a dye tracer); and just downstream of the diffuser. These samples were collected directly in the prescribed sample bottles (OMOE, 1989a and updates) and immediately submitted for analysis.

4.0 LABORATORY ANALYSIS

The effluent particulates and whole-water samples were analyzed at the Ministry's Laboratory Services Branch in Etobicoke for the individual parameters and scans listed in Table 1, according to documented procedures (OMOE, 1989b; OMOE, 1990; OMOEE, 1994b-d; OMOEE, 1995a-j; OMOEE, 1996c&d). The whole-water samples were each analyzed for 88 parameters, and the particulates for 136. The November 22-23 water samples were only analyzed for chlorinated aliphatics and aromatics.

Table 1. Sample analytical tests.

| Parameter or Scan | Whole-Water | Particulates |
|---|-------------|--------------|
| Moisture | | ✓ |
| Particle Size Distribution scan | | ✓ |
| Loss on Ignition | | ✓ |
| Carbon, total Organic | | ✓ |
| Carbon, dissolved Inorganic & dissolved Organic | ✓ | |
| Chloride | ✓ | ✓ |
| Nitrogen, total Kjeldahl | ✓ | ✓ |
| Arsenic | ✓ | ✓ |
| Cyanide, available | ✓ | ✓ |
| Mercury | ✓ | ✓ |
| Heavy Metals scan | ✓ | ✓ |
| Phenolics, reactive | ✓ | |
| Phosphorus, total | ✓ | ✓ |
| Potassium | | ✓ |
| Silicon | ✓ | ✓ |
| Sodium | | ✓ |
| Solvent Extractables (Oils & Greases) | ✓ | ✓ |
| Spectroscopic Identification of Unknowns by Infrared Spectroscopy | ✓ | ✓ |
| Residue, particulate (Suspended Solids) | ✓ | |
| Chlorinated Aliphatics and Aromatics scan | ✓ | ✓ |
| PCBs (total) & Organochlorine Pesticides scan | ✓ | ✓ |
| Polycyclic Aromatic Hydrocarbons scan | ✓ | ✓ |
| Polychlorinated Dibenzo- <i>p</i> -Dioxins and Dibenzofurans scan | | ✓ |
| Volatile Halocarbons and Hydrocarbons scan | | ✓ |

5.0 RESULTS AND DISCUSSION

Due to staffing limitations and the time required to collect sufficient particulate matter for analysis (i.e., about a day), only two collection periods could be scheduled. It was hoped that at least one of the collection periods would coincide with a period of high rainfall and runoff; however, the fixed nature of the survey schedule and the required setup time precluded this.

5.1 Contaminant Selection Criteria and Statistical Calculations

Data for individual effluent and effluent particulate samples as well as the number of detections per survey and overall detection frequencies are provided in Appendices A and B, respectively. Only those parameters detected in at least 50 % of samples from either of the two surveys were selected for inclusion in summary Tables 2 and 3. In calculating survey mean concentrations and loadings, values followed by “<=W” were assigned a value of zero; these were deemed “not detected” (i.e., not present above the minimum reportable value of the analytical method). Those values with a “<T” suffix were used as actual values. (The W value is 1.5 standard deviations of the mean for a series of low-level spiked samples; the Method Detection Limit (MDL) is 3 standard deviations. The T value is either 5 or 10 times the W value, depending on the analyte.) For convenience, the W value is referred to as the Minimum Reportable Value or “MRV” in the following discussion of results. Between the MDL and the T value, there is a 99 % confidence that the value is not a false positive; however, confidence in the actual concentration may not be as high. Above the T value, there is a greater than 99% confidence that the value is not a false positive and also a high degree of confidence that the analyte concentration is accurate.

The significance of differences between survey mean contaminant concentrations at the 95 % confidence level ($p < 0.05$) was determined using Student’s Paired t-Test. Correlation analysis (Pearson Product-Moment) was performed on transformed ($\log x+1$; $\arcsin\sqrt{x}$ for percentages) concentrations of selected parameters; correlations were deemed statistically significant at the 95 % confidence level (i.e., $p < 0.05$).

5.2 Effluent Whole-Water Contaminants Concentrations

Nine unfiltered effluent samples were collected during each of the two surveys. Table 2 summarizes analytical results for the 30 parameters detected in 50 % or more of the samples collected. Individual sample results are listed in Appendix A.

5.2.1 Detection Frequency

All of the “conventional” parameters, including chloride, nutrients, dissolved carbons, suspended solids, as well as many of the inorganics and heavy metals were detected in all 18 effluent samples (Table 2). Certain chlorinated aliphatics and aromatic contaminants were also consistently found in the Cole Drain effluent, specifically: hexachlorobutadiene (HCBd), pentachlorobenzene (PentaCB), hexachlorobenzene (HCB) and octachlorostyrene (OCS). In contrast, trace levels of hexachloroethane (HCE), 1,2,4- and 1,3,5-trichlorobenzene (TriCB) were present in most samples from the August survey, but were only found in one or two samples taken near the end of the June survey. Also, although quantifiable concentrations of solvent extractables were found in all samples from the first survey, they were undetected at a MRV of 0.5 mg.l^{-1} in the August effluent samples. Cadmium, with a MRV of $0.1 \text{ }\mu\text{g.l}^{-1}$, was only detected in one effluent sample from the June survey.

Table 2. Cole Drain effluent whole-water contaminants concentrations.

| Parameter | Concentration Units | Sampling Dates | | | | | | Sarnia WTP raw water, 1995 (n = 4) |
|-----------------------------|----------------------------|---------------------------|----------------------|------|----------------------------|----------------------|------|---|
| | | June 20-22, 1995 (n = 9) | | | August 21-24, 1995 (n = 9) | | | |
| | | Mean ± Std. Deviation. | No. of Detections | % CV | Mean ± Std. Deviation. | No. of Detections | % CV | |
| Calcium | mg.l ⁻¹ (ppm) | 28.0 ± 2 | 9 | 7.1 | -- | -- | -- | 27.7 ± 1.3 |
| *Chloride | " | 26.4 ± 1.9 | 9 | 7.2 | 40.3 ± 7.7 | 9 | 19 | 6.6 ± 0.4 |
| Carbon, dissolved Inorganic | " | 19.4 ± 0.2 | 9 | 1.0 | 19.8 ± 0.5 | 9 | 2.5 | 19.4 ± 0.7 |
| *Carbon, dissolved Organic | " | 3.4 ± 0.5 | 9 | 15 | 2.3 ± 0.3 | 9 | 13 | 1.5 ± 0.3 |
| Magnesium | " | 7.22 ± 0.39 | 9 | 54 | -- | -- | -- | 7.40 ± 0.30 |
| Nitrogen, total Kjeldahl | " | 0.34 ± 0.07 | 9 | 21 | 0.32 ± 0.03 | 9 | 9.4 | 0.19 ± 0.03 |
| *Phosphorus, total | " | 0.04 ± 0.01 | 9 | 25 | 0.09 ± 0.02 | 9 | 22 | 0.007 ± 0.010 |
| *Suspended Solids | " | 1.8 ± 0.5 | 9 | 28 | 3.7 ± 0.7 | 9 | 19 | 142 ± 0.5 |
| *Silicon | " | 0.48 ± 0.01 | 9 | 2.1 | 0.52 ± 0.02 | 9 | 3.8 | 0.61 ± 0.09 |
| * Solvent Extractables | mg.l ⁻¹ (ppm) | 1.1 ± 0.3 | 9 | 27 | 0 (0.5<W) | 0 | -- | -- |
| *Aluminum | µg.l ⁻¹ (ppb) | 89 ± 16 | 9 | 18 | 161 ± 36 | 9 | 22 | 25 ± 21 |
| *Barium | " | 13 ± 1 | 9 | 7.7 | 12 ± 0 | 9 | 0 | 15 ± 0.5 |
| *Chromium | " | 0.16 ± 0.17 | 5 | 106 | 0.56 ± 0.34 | 7 | 61 | 2.3 ± 0.54 |
| Cobalt | " | 1.5 ± 0.4 | 9 | 27 | 1.5 ± 0.4 | 9 | 27 | 0.04 ± 0.08 |
| *Copper | " | 1.6 ± 0.4 | 9 | 25 | 2.2 ± 0.5 | 9 | 23 | 0.85 ± 0.84 |
| *Iron | " | 33 ± 4 | 9 | 12 | 56 ± 13 | 9 | 23 | 33 ± 47 |
| *Manganese | " | 3.8 ± 0.5 | 9 | 13 | 22.1 ± 21.0 | 9 | 95 | 2.2 ± 2.5 |
| *Molybdenum | " | 1.1 ± 0.3 | 9 | 27 | 1.8 ± 0.4 | 9 | 22 | 0.50 ± 0.06 |
| *Nickel | " | 1.3 ± 0.4 | 9 | 31 | 4.6 ± 0.8 | 9 | 17 | 0.15 ± 0.30 |
| *Strontium | " | 98 ± 4 | 9 | 4.1 | 107 ± 5 | 9 | 4.7 | 101 ± 7 |
| Vanadium | " | 0.30 ± 0.31 | 5 | 103 | 0.53 ± 0.26 | 8 | 49 | 0.09 ± 0.07 |
| Zinc | " | 2.4 ± 1.7 | 9 | 71 | 3.0 ± 1.2 | 9 | 40 | 2.7 ± 2.1 |
| Phenolics, reactive | µg.l ⁻¹ (ppb) | 0.6 ± 0.2 <T | 9 | 33 | 1.8 ± 2.2 | 8 | 122 | 0.5 ± 0.6 |
| Hexachloroethane | ng.l ⁻¹ (ppt) | 0 (1<=W to 9<T) | 1 | -- | 2 ± 1 | 8 | 50 | 0 (1<=W) |
| *Hexachlorobutadiene | " | 256 ± 261 | 9 | 102 | 68 ± 12 | 9 | 14 | 0 (1<=W) |
| 1,2,4-Trichlorobenzene | " | 7 ± 13 | 2 | 186 | 6 ± 2 | 9 | 33 | 0 (5<=W) |
| *1,3,5-Trichlorobenzene | " | 0 (2<=W to 30) | 1 | -- | 4 ± 0 | 9 | 0 | 0 (5<=W) |
| Pentachlorobenzene | " | 19 ± 38 | 9 | 200 | 3 ± 1 | 9 | 33 | 0 (1<=W) |
| Hexachlorobenzene | " | 98 ± 249 | 9 | 254 | 5 ± 1 | 9 | 20 | 0 (1<=W) |
| Octachlorostyrene | " | 231 ± 591 | 9 | 256 | 3 ± 1 | 9 | 33 | 0 (1<=W) |

NOTES: Concentrations provided are arithmetic means and standard deviations.
 CV = Coefficient of Variation = (Std. Dev'n./Mean) x 100.
 Samples with no detectable concentrations were assigned "zero" for statistical purposes.
 ' -- ' = no sample or analytical results, or CV could not be calculated.
 ' * ' = June and August survey means are significantly different (Student's Paired t-Test, p < 0.05).
 Sarnia WTP data from OMOEE (1996a).
 Parameter mean concentrations in shaded cells are higher than the means of 1995 Sarnia (Lambton Area) WTP raw water samples.

Parameters not detected in any effluent samples from either survey included: arsenic, beryllium, lead, mercury and titanium, with MRVs of 1.0, 0.1, 5.0, 0.02 and 1.0 µg.l⁻¹, respectively; all organochlorine pesticides, PCBs, trichlorotoluenes, tetrachlorobenzenes or 1,2,3-TriCB, with MRVs of 1 to 5 ng.l⁻¹ (20 ng.l⁻¹ for total PCBs); and all polycyclic aromatic hydrocarbons (PAHs), with MRVs of 0.2 to 1.0 µg.l⁻¹.

5.2.2 Survey Concentrations and Variability

Concentrations of selected parameters in individual samples are shown in Figures 3 through 7. The August survey mean effluent concentrations of chloride, phosphorus, suspended solids, aluminum, chromium, manganese, nickel and phenolics were from two- to six-fold higher than in June. In contrast, mean HCBd, PentaCB, HCB and OCS concentrations during the June survey were from three- to 75-fold (e.g., OCS) higher than in the second survey (Table 2), partly due to higher concentrations in the 12:40 PM sample of June 21 (Appendix A, Table A-3). The higher mean concentrations and large standard deviations of these four chlorinated organics also resulted from the elevated concentrations found in samples from the first half of the June survey (Fig. 7). Despite the differences between the survey means, only the mean concentrations of chloride, DOC, phosphorus, suspended solids, silicon, solvent extractables, aluminum, barium, chromium, copper, iron, manganese, molybdenum, nickel, strontium, HCBd and 1,3,5-TriCB differed significantly ($p < 0.05$) between the June and August surveys. Of these parameters, mean concentrations of all but DOC, barium, solvent extractables and HCBd were significantly higher ($p < 0.05$) in the August survey (Table 2).

The high trace organic concentrations did not seem to be correlated with the concentration of suspended solids (RSP) in the effluent (Appendix A, Table A-6). In fact, scatter plots and correlation analysis of the complete data set indicated a statistically significant ($p < 0.05$; $n = 18$) negative linear correlation between the concentrations of HCBd, PentaCB and OCS that and of suspended solids or RSP ($r = -0.48$ to -0.66). There was however, a significant positive correlation between the concentrations of organics (HCBd, PentaCB, HCB and OCS) and of dissolved organic carbon or DOC ($r = 0.47$ to 0.69), related to the significant negative correlation between DOC and RSP concentrations ($r = -0.79$) (Fig. 8). In contrast to these organics, concentrations of a number of inorganics and metals exhibited a significant positive correlation with RSP levels, the strongest being for aluminum, phosphorus, chloride, iron, nickel and strontium ($r = 0.73$ to 0.92). Overall as well as for the June survey, significant positive correlations were noted between HCBd, PentaCB, HCB and OCS concentrations ($r = 0.91$ to 0.99), but this was not evident during the August survey, in which only HCBd and OCS concentrations were strongly correlated (Appendix A, Table A-6).

The coefficients of variation (CV) for conventional parameters (Table 2) were usually somewhat higher than the CVs reported for laboratory duplicate analyses (Janhurst, 1996), suggesting that the observed concentration variability was the result of field temporal variation, and not analytical variability. Parameters with CVs above 90 % included: chromium, vanadium, HCBd, 1,2,4-TriCB, PentaCB, HCB and OCS during the June survey; and manganese and phenolics in the August survey. This high variability was due either to a number of samples with parameter concentrations below the respective MRVs which were assigned a value of zero for statistical calculations (i.e., chromium, vanadium, 1,2,4-TriCB), or a few samples with quite high concentrations (i.e., manganese, phenolics, HCBd, PentaCB, HCB, OCS). Such high sample-to-sample variation has been observed previously. For example, twice-weekly monitoring of Sarnia organic chemical industry effluents during 1986/87 found that the Cole Drain discharge had the

Figure 3. Cole Drain effluent whole-water (bars & left vertical axis) and particulates (lines & right vertical axis) concentrations of inorganic and organic carbon, calcium, chloride, Kjeldahl nitrogen and phosphorus.

Figure 4. Cole Drain effluent whole-water (bars & left vertical axis) and particulates (lines & right vertical axis) concentrations of phenolics, solvent extractables, suspended solids and silicon.

Figure 5. Cole Drain effluent whole-water (bars & left vertical axis) and particulates (lines & right vertical axis) concentrations of aluminum, chromium, cobalt, copper, iron and manganese.

Figure 6. Cole Drain effluent whole-water (bars & left vertical axis) and particulates (lines & right vertical axis) concentrations of mercury, nickel, strontium and zinc.

Figure 7. Cole Drain effluent whole-water (bars & left vertical axis) and particulates (lines & right vertical axis) concentrations of hexachlorobutadiene, 1,3,5-trichlorobenzene, pentachlorobenzene, hexachlorobenzene, octachlorostyrene and Total PCBs. Note difference in concentration axes for compounds (linear vs. logarithmic).

Figure 8. Relationship of Cole Drain effluent whole-water concentrations of selected inorganics, nutrients, heavy metals and organics to suspended solids and dissolved organic carbon concentrations. Note difference in concentration units for dissolved organic carbon (DOC). Lines are linear regressions of best-fit.

highest and most variable concentrations of chlorinated benzenes, toluenes and OCS, with concentrations varying by up to three orders of magnitude between successive samples (St. Clair River MISA, 1991b). The 1986/87 study also concluded that concentrations of HCB and suspended solids in the final effluent were significantly correlated with rainfall.

Concentrations of HCB, PentaCB, HCB and OCS in some of the June and August effluent samples were similar to levels found within the discharge plume of the diffuser in November, 1995 (see Table 7), as well as to the means of 1989/90 samples from the Cole Drain and the Polysar Biox plant effluent (Tuszynski, 1992).

The mean 1995 Cole Drain effluent concentrations of chloride, DOC, total Kjeldahl nitrogen, total phosphorus, aluminum, cobalt, copper, iron, manganese, molybdenum, nickel, vanadium, zinc, HCE, HCB, 1,2,4,-TriCB, PentaCB, HCB and OCS were from two- to over 200-fold higher than the means for 1995 upstream raw water samples from the Sarnia (Lambton Area) Water Treatment Plant intake (OMOEE, 1996a). (This facility withdraws Lake Huron water to supply Lambton County.) The mean concentrations of aluminum, cobalt, copper, manganese, molybdenum, nickel, vanadium, 1,2,4-TriCB, PentaCB and HCB in the Cole Drain effluent were also higher than the means of samples collected from the open waters of Lake Huron during 1986 (Stevens & Neilson, 1989) and 1981 (Rossman & Barres, 1988). Of the above parameters, chloride, total Kjeldahl nitrogen, total phosphorus, copper, manganese, nickel, zinc, HCB, HCB and OCS are on the “Contaminants of Concern” list identified by the St. Clair River Remedial Action Plan process (St. Clair River RAP, 1995). (This list includes those contaminants which have exceeded Ontario, Michigan or Great Lakes Water Quality Agreement objectives or standards for water, sediment or aquatic biota. It was compiled during the RAP Stage 1 phase to assist in: determining the potential impact from existing sources and assessing the need for additional remediation; and measuring progress towards the virtual elimination of persistent toxic substances within a philosophy of zero discharge. “Yardstick” values were derived from a review of information from five principal jurisdictions or agencies: Ontario, Michigan, Canada, United States and the International Joint Commission. The RAP Yardsticks usually represent the lowest, scientifically valid number available for a contaminant. They were proposed as the concentrations to be achieved in water, sediment and biota as a result of RAP implementation). HCB is also on the OMOE list for bans, phase-outs or reductions (Socha *et al.*, 1992) and of potential endocrine-disrupting contaminants (Socha, 1996) as is OCS (JEA, 1998).

5.3 Effluent Particulate-Associated Contaminants Concentrations

In June, effluent particulates were collected over two time periods, resulting in replicate samples of 68 and 102 grams wet weight, respectively. In the August survey, particulates were collected over three periods, resulting in replicate samples weighing 130 g, 241 g (analyzed as split samples of 95 g and 146 g), and 175 g (splits of 65 and 110 g), respectively. Table 3 summarizes analytical results for the 52 parameters (as well as three summary parameters) detected in at least one of the particulates samples collected. Individual analytical results for both the replicate and

Figure 9. Size distribution of Cole Drain effluent particulates.

the split samples are listed in Appendix B.

Diffuse reflectance Fourier transform infrared spectroscopy detected the presence of humic acids in all particulates samples. Humic acids are a component of many soils and sediments due to the decomposition of plant material (Buckman & Brady, 1969; Håkanson & Jansson, 1983).

Particle size distribution analysis indicated that the effluent particulates were primarily composed of fine sand to very fine clay, ranging in diameter from 176 μm to $< 0.21 \mu\text{m}$ (Appendix B, Table B-1). Particle size distribution was usually unimodal, with medium to coarse silt (median diameter: 38 μm ; range: 24 to 42 μm) in greatest abundance; however, coarse silt with a median diameter of 52 μm predominated in the June 22nd sample (Table 3 and Fig. 9). Such fine particles have a high surface-to-volume ratio which, in combination with their relatively high organic carbon content (range: 92 to 120 g.kg^{-1} , or 9.2 to 12 %), provides a suitable site or matrix for the adsorption of hydrophobic contaminants with high particulate (K_p) and organic carbon (K_{oc}) partition coefficients (Förstner & Wittmann, 1983; Fletcher & McKay, 1993; Mackay *et al.*, 1992a & b).

5.3.1 Detection Frequency

All of the conventional parameters, as well as most inorganics, heavy metals and chlorinated aliphatics and aromatics were detected in the five different particulates samples.

It is noteworthy that 14 of the 16 unsubstituted PAH compounds analyzed for in particulates were found in at least one of the samples (Fig. 10), whereas the MRVs for these compounds in the whole-water effluent samples were not low enough to detect their presence (see Section 5.2.1). Assuming that these PAHs are entirely associated with the particulate phase and multiplying by the effluent suspended solids concentrations, yields equivalent whole-water concentrations of from 0.09 to 0.54 ng.l^{-1} during the June survey, and 0.07 to 1.06 ng.l^{-1} in the August survey. (This, however, is likely an underestimate of the final effluent concentrations, since all PAHs, particularly the lower molecular weight compounds (e.g., naphthalene, acenaphthene) could be present in the aqueous phase.) These concentrations are about three orders of magnitude lower than the MRVs of the method employed for analysis of the whole-water effluent samples (200 to 1000 ng.l^{-1}). In 1985, concentrations of individual PAHs in Cole Drain samples ranged from 14 to 160 ng.l^{-1} (EC & OMOE, 1986), considerably higher than the above whole-water estimates, but below the MRVs for the 1995 samples. Also, during 1995 no PAHs were detected in any upstream raw water samples (MRVs from 1 to 50 ng.l^{-1}) collected at the Sarnia (Lambton Area) WTP (OMOEE, 1996a).

As with the PAHs, PCBs resembling a mixture of Aroclors 1254 and 1260 were detected in all particulates samples, but not in the whole-water samples. This was again probably due to the relatively high MRV (20 ng.l^{-1}) for total PCBs in liquid samples.

Representatives of all tetra-, penta-, hexa-, hepta- and octachlorinated dioxin and dibenzofuran homolog groups, as well as 14 of the 15 toxic (2,3,7,8-substituted) isomers were detected in one

Table 3. Cole Drain effluent particulate-associated contaminants concentrations.

| Parameter | Concentration Units | Sampling Dates | | | | | | Point Edward (Sarnia WTP) particulates, 1995 (n =18) |
|-----------------------------------|---------------------------|----------------------------|-------------------|------|----------------------------|-------------------|------|--|
| | | June 20-22, 1995 (n = 2) | | | August 21-24, 1995 (n = 3) | | | |
| | | Mean & (Minimum & Maximum) | No. of Detections | % CV | Mean ± Standard Deviation | No. of Detections | % CV | |
| Moisture | % | 77 (76 - 78) | 2 | 1.8 | 78 ± 2 | 3 | 2.6 | -- |
| Sand, <2000 - >62 µm | % | 23.5 (10.0 - 37.0) | 2 | 81 | 25.8 ± 3.6 | 3 | 14 | -- |
| Silt, <62 - >3.73 µm | % | 66.1 (54.8 - 77.3) | 2 | 24 | 65.1 ± 3.2 | 3 | 4.9 | -- |
| Clay, <3.73 - >0.17 µm | % | 10.2 (8.1 - 12.3) | 2 | 29 | 9.1 ± 0.7 | 3 | 7.7 | -- |
| Median Particle Size | µm | 37.9 (24.0 - 51.8) | -- | 52 | 37.8 ± 3.5 | -- | 9.3 | -- |
| Calcium | mg.kg ⁻¹ (ppm) | 47000 (44000 - 50000) | 2 | 9.0 | 43000 ± 3464 | 3 | 8.1 | -- |
| Chloride | " | 406 (63 - 750) | 2 | 119 | 120 ± 8.7 | 3 | 7.2 | -- |
| Carbon, total Organic | g.kg ⁻¹ (ppth) | 106 (92 - 120) | 2 | 19 | 110 ± 8.7 | 3 | 7.9 | -- |
| Loss on Ignition | " | 230 (200 - 260) | 2 | 18 | 246.7 ± 5.8 | 3 | 2.3 | -- |
| Magnesium | mg.kg ⁻¹ (ppm) | 20500 (19000 - 22000) | 2 | 10 | 18333 ± 1443 | 3 | 7.9 | -- |
| Nitrogen, total Kjeldahl | g.kg ⁻¹ (ppth) | 15.0 (13 - 17) | 2 | 19 | 15.8 ± 1.0 | 3 | 6.6 | -- |
| *Phosphorus, total | " | 12.0 (12 - 12) | 2 | 0.0 | 16.7 ± 1.5 | 3 | 9.1 | -- |
| Potassium | mg.kg ⁻¹ (ppm) | 2850 (2700 - 3000) | 2 | 7.4 | 2467 ± 115 | 3 | 4.7 | -- |
| *Sodium | " | 360 (360 - 360) | 2 | 0.0 | 528 ± 16.1 | 3 | 3.0 | -- |
| Solvent Extractables (Oil&Grease) | " | 18795 (14885 - 22706) | 2 | 29 | 13374 ± 200 | 3 | 1.5 | -- |
| *Aluminum | mg.kg ⁻¹ (ppm) | 37000 (37000 - 37000) | 2 | 0.0 | 49500 ± 1323 | 3 | 2.7 | -- |
| Arsenic | " | 7.15 (7.1 - 7.2) | 2 | 1.0 | 7.05 ± 0.22 | 3 | 3.1 | -- |
| Barium | " | 88.5 (82 - 95) | 2 | 10 | 89.2 ± 1.6 | 3 | 1.8 | -- |
| Beryllium | " | 0 (0.5<W - 0.6) | 1 | -- | 0 (0.5<W) | 0 | -- | -- |
| Cadmium | " | 1.35 (1.1 - 1.6) | 2 | 26 | 2.65 ± 0.33 | 3 | 12 | -- |
| *Chromium | " | 99.5 (89 - 110) | 2 | 15 | 168.3 ± 2.9 | 3 | 1.7 | -- |
| *Cobalt | " | 76 (74 - 78) | 2 | 3.7 | 89.5 ± 2.3 | 3 | 2.6 | -- |
| Copper | " | 440 (280 - 600) | 2 | 51 | 170.8 ± 64.4 | 3 | 38 | -- |
| Iron | " | 20000 (19000 - 21000) | 2 | 7.1 | 17500 ± 866 | 3 | 4.9 | -- |
| Lead | " | 71 (52 - 90) | 2 | 38 | 41.3 ± 6.0 | 3 | 14 | -- |
| *Manganese | " | 570 (550 - 590) | 2 | 5.0 | 408.3 ± 27.5 | 3 | 6.7 | -- |
| *Mercury | " | 0.25 (0.25 - 0.26) | 2 | 2.8 | 0.45 ± 0.02 | 3 | 4.4 | -- |
| Molybdenum | " | 4.0 (2.4<T - 6.6) | 2 | 66 | 3.65 ± 0.43 | 3 | 12 | -- |
| *Nickel | " | 104.5 (99 - 110) | 2 | 7.4 | 151.7 ± 2.9 | 3 | 1.9 | -- |
| Strontium | " | 65.5 (65 - 66) | 2 | 1.1 | 82.2 ± 9.1 | 3 | 11 | -- |
| *Titanium | " | 135 (130 - 140) | 2 | 5.2 | 117 ± 5.8 | 3 | 5.0 | -- |
| Vanadium | " | 29 (27 - 31) | 2 | 9.7 | 24.5 ± 1.3 | 3 | 5.3 | -- |
| Zinc | " | 265 (240 - 290) | 2 | 13 | 320 ± 8.7 | 3 | 2.7 | -- |
| *Hexachloroethane | µg.kg ⁻¹ (ppb) | 7 (6 - 8) | 2 | 20 | 14.7 ± 0.3 | 3 | 2.0 | -- |
| Hexachlorobutadiene | " | 5700 (3600 - 7800) | 2 | 52 | 1983 ± 176 | 3 | 8.9 | 0.80 ± 0.80 |
| 1,2,4-Trichlorobenzene | " | 28.0 (20 - 36) | 2 | 40 | 29.3 ± 0.6 | 3 | 2.0 | 0 (<3.6) |
| *1,3,5-Trichlorobenzene | " | 15.0 (14 - 16) | 2 | 9.4 | 78.7 ± 9.2 | 3 | 12 | 0.92 ± 1.27 |
| 1,2,3,5-Tetrachlorobenzene | " | 28.5 (26 - 31) | 2 | 12 | 28.3 ± 2.9 | 3 | 10 | 0 (<2.7) |
| 1,2,4,5-Tetrachlorobenzene | " | 45.5 (37 - 54) | 2 | 26 | 48.3 ± 2.9 | 3 | 6.0 | 0 (<2.7) |
| Pentachlorobenzene | " | 290 (200 - 380) | 2 | 44 | 122 ± 15.2 | 3 | 12 | 0.53 ± 0.58 |
| Hexachlorobenzene | " | 1575 (650 - 2500) | 2 | 83 | 455 ± 57.7 | 3 | 13 | 1.03 ± 2.32 |
| Octachlorostyrene | " | 4050 (1200 - 6900) | 2 | 99 | 695 ± 120 | | 17 | 0 (<4.2) |
| Total PCBs | " | 560 (320 - 800) | 2 | 61 | 123 ± 40 | 3 | 33 | -- (74 in 1987-89) |
| *Acenaphthene | µg.kg ⁻¹ (ppb) | 60 (40 - 80) | 2 | 47 | 0 (20<=W) | 0 | -- | 0 (<10) |
| Anthracene | " | 50 (40 - 60) | 2 | 71 | 73 ± 5.8 | 3 | 7.9 | -- |
| Benzo(a)anthracene | " | 100 (80 - 120) | 2 | 28 | 133 ± 25 | 3 | 19 | -- |
| Benzo(b)fluoranthene | " | 140 (120 - 160) | 2 | 20 | 137 ± 25 | 3 | 18 | -- |
| Benzo(k)fluoranthene | " | 50 (40 - 60) | 2 | 28 | 60 ± 35 | 3 | 58 | -- |
| Benzo(g,h,i)perylene | " | 100 (80 - 120) | 2 | 28 | 107 ± 12 | 3 | 11 | -- |

| Parameter | Concentration Units | Sampling Dates | | | | | | Point Edward (Sarnia WTP) particulates, 1995 (n=18) |
|----------------------------|---------------------------|----------------------------|-------------------|------|----------------------------|-------------------|------|---|
| | | June 20-22, 1995 (n = 2) | | | August 21-24, 1995 (n = 3) | | | |
| | | Mean & (Minimum & Maximum) | No. of Detections | % CV | Mean ± Standard Deviation | No. of Detections | % CV | |
| Benzo(a)pyrene | µg.kg ⁻¹ (ppb) | 100 (80 - 120) | 2 | 28 | 113 ± 12 | 3 | 10 | -- |
| Chrysene | " | 210 (180 - 240) | 2 | 20 | 210 ± 30 | 3 | 14 | -- |
| Dibenzo(a,h)anthracene | " | 60 (40<=W - 120) | 1 | 141 | 20 ± 35 | 1 | 173 | -- |
| Fluoranthene | " | 300 (220 - 380) | 2 | 38 | 280 ± 72 | 3 | 26 | 73 ± 133 |
| *Indeno(1,2,3-cd)pyrene | " | 100 (80 - 120) | 2 | 28 | 287 ± 12 | 3 | 4.0 | -- |
| Naphthalene | " | 50 (40 - 60) | 2 | 14 | 53 ± 6 | 3 | 11 | -- |
| Phenanthrene | " | 240 (200 -280) | 2 | 24 | 247 ± 35 | 3 | 14 | 82 ± 112 |
| Pyrene | " | 300 (220 - 380) | 2 | 38 | 283 ± 55 | 3 | 12 | 62 ± 99 |
| Total of 16 PAHs | " | 1860 (1580 - 2140) | -- | 22 | 2003 ± 268 | -- | 13 | -- |
| Total PCDD/F Homologs | ng.kg-1 (ppt) | 2732 (1502 - 3962) | -- | 64 | 1804 ± 271 | -- | 15 | -- |
| Total 2,3,7,8-TetraCDD TEQ | " | 17 (12 -23) | -- | 42 | 23 ± 2.1 | -- | 9.0 | -- |

NOTES: Concentrations are arithmetic means and standard deviations.
CV = Coefficient of Variation = (Std. Dev'n./Mean) x 100; or for n = 2, CV = [$\sqrt{2}(\text{max.} - \text{min.})/(\text{max.} + \text{min.})$] x 100.
Samples with no detectable concentrations were assigned "zero" for calculation purposes.
'--' = no sample or analytical result; CV could not be calculated; or not appropriate.
'*' = survey means are significantly different (Student's Paired t-Test, p < 0.05).
'NC' = could not be calculated (mean concentration below method reporting limits).
'NS' = matrix not sampled for this parameter.
Point Edward data from Chan & Harrison (1997); samples collected at Sarnia WTP intake.
Mean concentrations of parameters in shaded cells are higher than the means of 1995 (1987-89 for total PCBs) Point Edward particulate samples.

or more of the particulates samples (see Appendix B, Table B-6). The latter included 2,3,7,8-TetraCDF, at concentrations of 11 to 31 ng.kg⁻¹, or ppt. These compounds, as well as PCBs and PAHs, are on the St. Clair River Remedial Action Plan Contaminants of Concern list (St. Clair River RAP, 1995).

Contaminants not detected in any particulates samples included the trichlorotoluenes, 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene and all organochlorine pesticides (MRV of 1 to 5 µg.kg⁻¹), acenaphthylene and fluorene (MRV = 20 µg.kg⁻¹) and 2,3,7,8-TetraCDD (MRVs of 1 to 5 ng.kg⁻¹). Although no target volatile hydrocarbons were detected in any of the particulates samples (MRVs of 10 to 20 µg.kg⁻¹), the headspace analysis did detect trace levels of "non-target medium boiling point hydrocarbons" in all samples from the August survey. Such compounds include a variety of non-halogenated hydrocarbons, such as those associated with petroleum.

5.3.2 Survey Concentrations and Variability

The average June survey concentrations of chloride, copper, lead, HCBd, PentaCB, HCB, OCS, total PCBs, acenaphthene, and total PCDD/F congeners on particulates were from two- to six-fold higher than in August. In contrast, the August mean concentrations of cadmium, chromium, mercury, HCE, 1,3,5-trichlorobenzene and indeno(1,2,3-cd)pyrene were from about two- to five-fold higher than in June. Nevertheless, only the means of phosphorus, sodium, aluminum, chromium, cobalt, manganese, mercury, nickel, titanium, HCE, 1,3,5-TriCB, acenaphthene and indeno (1,2,3-cd)pyrene were significantly different between surveys (p < 0.05). Of these, all but manganese, titanium and acenaphthene had higher mean concentrations during the August survey (Table 3).

Figure 10. Cole Drain effluent particulates concentration of Total PAHs, and overall mean PAH compound profile. Horizontal bars in upper figure represent particulate concentrations and “NDs” relate to whole-water effluent samples; PAH compounds in lower figure are listed in order of decreasing water solubility, from left to right (Mackay *et al.*, 1992b).

Figure 11. Cole Drain effluent particulates concentrations of Total PCDD/F homologs (solid lines & left vertical axis) and 2,3,7,8-TetraCDD TEQ (dashed lines & right vertical axis), and overall mean PCDD/F homolog and isomer profiles. Homolog groups are listed in order of decreasing water solubility and increasing organic carbon partition coefficient, from left to right.

Of the 16 PAHs analyzed for, phenanthrene, fluoranthene and pyrene dominated the concentration profile of particulates samples, followed by chrysene and indeno(1,2,3-cd)pyrene (Fig. 10).

Individual sample concentrations of the Cl₄ to Cl₈ polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) homolog groups and of the 2,3,7,8-substituted isomers are provided in Appendix B, Table B-6. Overall, the concentration profile of PCDD/Fs in the particulates was dominated by OctaCDD and OctaCDF (Fig. 11). The nearly two-fold higher concentration of the latter compound suggests a contribution from vinyl chloride monomer or polyvinyl chloride manufacturing wastes (Carroll *et al.*, 1997). Also, the greater abundance of 1,2,3,4,7,8-HexaCDF relative to 1,2,3,6,7,8-HexaCDF, particularly in the June 21 sample, indicates a contribution from commercial PCBs (i.e., Aroclors), which had their highest concentration in this sample (see Appendix B, Table B-4). There may also be a contribution from sewage sludge, as suggested by the higher concentration of 1,2,3,4,6,7,8-HeptaCDD relative to the lower-chlorinated isomers (Cleverly, 1997). The Toxic Equivalencies (i.e., toxicity relative to 2,3,7,8-TetraCDD, the most toxic isomer) of the 2,3,7,8-substituted isomers were calculated using the International Toxic Equivalence Factors, or I-TEFs (Safe, 1990; Rappe, 1994) and summed. The mean Total 2,3,7,8-TetraCDD TEQs for the June and August surveys, 17 and 23 ng.kg⁻¹ (ppt), constituted 0.6 and 1.3 %, respectively, of the Total PCDD/F homolog group concentrations of 2732 and 1804 ng.kg⁻¹. (Recently, new TEFs have been proposed by the World Health Organization (WHO, 1997). These increase the TEF for 1,2,3,7,8-PentaCDD and lower those for OctaCDD and OctaCDF ; consequently, their use would change the Total TEQs for these samples by very little.)

The small number of particulates samples (n = 5) limited the number of significant correlations between analytical parameters. Overall, statistically significant positive correlations (p < 0.05) were found between HCBd, PentaCB, HCB, OCS, total PCBs and solvent extractables concentrations (r = 0.90 to 1.00) and between these organics and several heavy metals, particularly lead (r = 0.89 to 0.98). However, correlations between these organics and the concentrations of HCE, TriCBs and TetraCBs ranged from low to significantly negative in the case of 1,3,5-TriCB (Appendix B, Table B-9). Also, no significant correlations were detected between the concentrations of HCBd, PentaCB, HCB, OCS and total PCBs and with the total organic carbon (TOC) content or proportion of fines (i.e., silt or clay) in the particulates.

Coefficients of variation for most parameters in the replicate particulates samples (Table 3) were usually higher than the CVs for split samples from the August survey (see Appendix B, Table B-10), suggesting that the variability was related to actual temporal variation in concentrations, and not to sample handling and/or analytical variability. However, the reverse was the case for aluminum, cadmium, cobalt, HCE, 1,2,4- and 1,3,5-TriCB, benzo(g,h,i)perylene and naphthalene (Table 3). The higher variability in contaminants concentrations, particularly during the June survey, may be due to the greater variability of median particle size diameter between the two samples from this survey (see Table 3 and Appendix B, Table B-1).

Information was available only for a limited number of organic contaminants on particulates collected upstream at Point Edward (from the Sarnia (Lambton Area) WTP intake), during 1995 (Chan & Harrison, 1997). Comparison with this data indicated that the mean concentrations of (at least) HCBd, 1,2,4-TriCB, 1,3,5-TriCB, 1,2,3,5-TetraCB, 1,2,4,5-TetraCB, PentaCB, HCB, OCS, fluoranthene, phenanthrene and pyrene were from 4 to over 7000-fold higher on Cole Drain effluent particulates than on the upstream (i.e., Lake Huron) particulates (see Table 3). Total PCBs concentrations on 1995 Cole Drain particulates were also higher than on upstream particulates from the period 1987/89 (Chan, 1993). Of the above compounds, HCBd, HCB, OCS, PCBs and the PAHs were identified as Contaminants of Concern by the St. Clair River Remedial Action Plan (St. Clair River RAP, 1995 - see Section 5.2.2). Also included on this list are the PCDDs and PCDFs, of which all homologs and most toxic isomers were found on all particulates samples (Section 5.3.1).

5.4 Contaminants Loadings

Flow rate data were not available for the individual sampling dates or times of the 1995 study. Consequently, loadings of contaminants to the St. Clair River from the Cole Drain were calculated as a product of the mean or average concentrations listed in Tables 2 and 3 and the long-term (October 1/89 through September 30/90) mean daily flow rate of 117 937 m³.d⁻¹. This flow rate is the sum of the mean Bayer (previously Polysar) Biox Plant effluent (12 425 m³.d⁻¹) and mean Cole Drain (105 475 m³.d⁻¹) flow rates measured during the MISA pre-regulation monitoring period (Tuszynski, 1992). The 1989/90 Cole Drain flow rate is similar to the 102 000 m³.d⁻¹ measured on November 21, 1995 by Ministry staff (G. Szober, OMOE Sarnia District Office, pers. comm., 1995). Loadings of particulate-associated contaminants were calculated using the corresponding mean suspended solids concentration for whole water effluent samples (Table 2), the contaminant concentration (Table 3), and the above 1989-90 mean daily flow rate.

It should be emphasized that the calculated 1995 Cole Drain loadings are “estimated gross” daily loadings, since the intake water loadings of facilities discharging to the drain have not been subtracted, and sampling only extended over two three-day periods. For those contaminants with no detectable concentration or a mean concentration below the MRV, loadings were calculated using half the analytical MRV to provide an estimate of the loading. This is midway between using zero (best case) or the actual MRV (worst case).

5.4.1 *Relative Magnitude of Loadings*

Estimated daily loadings are provided as June and August survey means in Table 4. These results show that whole-water based loadings of the conventional parameters were the greatest. In decreasing magnitude, these include: chloride, calcium and dissolved inorganic carbon, ranging from 4.7 to 2.3 tonnes.d⁻¹; dissolved organic carbon, magnesium, suspended solids and solvent extractables, at 850 to 130 kilograms.d⁻¹; and nutrients, including nitrogen, phosphorus and silicon, ranging from 60 to 7.5 kg.d⁻¹.

Table 4. Summary of Cole Drain effluent contaminants loadings.

| Parameter | Loading Units | Sampling Periods | | | | | |
|-------------------------------------|--------------------|------------------|--------------|---------------|--------------------|--------------|---------------|
| | | June 20-22, 1995 | | | August 21-24, 1995 | | |
| | | Whole-Water | Particulates | %Particulates | Whole-Water | Particulates | %Particulates |
| Calcium | kg.d ⁻¹ | 3302. | 9.98 | 0.3 | NS | 18.8 | -- |
| Chloride | " | 3114. | 0.086 | 0.002 | 4753. | 0.052 | 0.001 |
| Carbon, dissolved Inorganic | " | 2288. | NS | -- | 2335. | NS | -- |
| Carbon, dissolved Organic | " | 401. | NS | -- | 271. | NS | -- |
| Carbon, total Organic | " | NS | 22.5 | -- | NS | 48.0 | -- |
| Loss on Ignition | " | NS | 48.8 | -- | NS | 108. | -- |
| Magnesium | " | 852. | 4.35 | 0.5 | -- | 8.00 | -- |
| Nitrogen, total Kjeldahl | " | 40.1 | 3.18 | 7.9 | 37.7 | 6.89 | 18 |
| Phosphorus, total | " | 7.46 | 4.03 | 54 | 16.8 | 11.5 | 68 |
| Potassium | " | NS | 0.61 | -- | NS | 1.08 | -- |
| Silicon | " | 56.6 | NS | -- | 61.3 | NS | -- |
| Sodium | " | NS | 0.075 | -- | NS | 0.230 | -- |
| Suspended Solids | " | 212. | NS | -- | 436. | NS | -- |
| Solvent Extractables (Oil & Grease) | " | 130. | 3.99 | 3.1 | 0 (29.5) | 5.84 | ≤ 100 (20) |
| Aluminum | g.d ⁻¹ | 10496. | 7855. | 75 | 18988. | 21600. | 114 |
| Arsenic | " | 0 (59.0) | 1.52 | ≤ 100 (2.6) | 0 (59.0) | 3.08 | ≤ 100 (5.2) |
| Barium | " | 1533. | 18.8 | 1.2 | 1415. | 38.9 | 2.7 |
| Beryllium | " | 0 (5.90) | 0 (0.053) | -- (0.9) | 0 (5.90) | 0 (0.109) | -- (1.8) |
| Cadmium | " | 0 (5.90) | 0.287 | ≤ 100 (4.9) | 0 (5.90) | 1.16 | ≤ 100 (20) |
| Chromium | " | 18.9 | 21.1 | 112 | 66.0 | 73.4 | 111 |
| Cobalt | " | 177. | 16.1 | 9.1 | 177. | 39.1 | 22 |
| Copper | " | 189. | 93.4 | 49 | 259. | 74.5 | 29 |
| Iron | " | 3892. | 4246. | 109 | 6604. | 7636. | 116 |
| Lead | " | 0 (295) | 15.1 | ≤ 100 (5.1) | 0 (295) | 18.0 | ≤ 100 (6.1) |
| Manganese | " | 448. | 121. | 27 | 2606. | 178. | 6.8 |
| Mercury | " | 0 (1.179) | 0.053 | ≤ 100 (4.4) | 0 (1.179) | 0.196 | ≤ 100 (17) |
| Molybdenum | " | 130. | 0.849 | 0.7 | 212. | 1.59 | 0.8 |
| Nickel | " | 153. | 22.2 | 15 | 542. | 66.2 | 12 |
| Strontium | " | 11558. | 13.9 | 0.1 | 12619. | 35.9 | 0.3 |
| Titanium | " | 0 (59.0) | 28.9 | ≤ 100 (49) | 0 (59.0) | 50.9 | ≤ 100 (86) |
| Vanadium | " | 35.4 | 6.16 | 17 | 62.5 | 10.7 | 17 |
| Zinc | " | 283. | 56.3 | 20 | 354. | 140. | 40 |
| Phenolics | g.d ⁻¹ | 70.8 | NS | ≤ 100 | 212. | NS | ≤ 100 |
| Hexachloroethane | g.d ⁻¹ | 0 (0.059) | 0.001 | ≤ 100 (1.7) | 0.236 | 0.006 | 2.5 |
| Hexachlorobutadiene | " | 30.192 | 1.210 | 4.0 | 8.020 | 0.865 | 11 |
| 1,2,4-Trichlorobenzene | " | 0.826 | 0.006 | 0.7 | 0.708 | 0.013 | 1.8 |
| 1,3,5-Trichlorobenzene | " | 0 (0.118) | 0.003 | ≤ 100 (2.5) | 0.472 | 0.034 | 7.2 |
| 1,2,3,5-Tetrachlorobenzene | " | 0 (0.059) | 0.006 | ≤ 100 (10) | 0 (0.059) | 0.012 | ≤ 100 (20) |
| 1,2,4,5-Tetrachlorobenzene | " | 0 (0.059) | 0.010 | ≤ 100 (17) | 0 (0.059) | 0.021 | ≤ 100 (36) |
| Pentachlorobenzene | " | 2.241 | 0.062 | 2.7 | 0.354 | 0.053 | 15 |
| Hexachlorobenzene | " | 11.558 | 0.334 | 2.9 | 0.590 | 0.199 | 34 |
| Octachlorostyrene | " | 27.244 | 0.860 | 3.2 | 0.354 | 0.303 | 86 |
| PCBs, total | " | 0 (1.179) | 0.119 | ≤ 100 (10) | 0 (1.179) | 0.054 | ≤ 100 (4.6) |
| Acenaphthene | g.d ⁻¹ | 0 (11.794) | 0.013 | ≤ 100 (0.1) | 0 (11.794) | 0 (0.0004) | -- (~0) |
| Acenaphthylene | " | " | 0 (0.0002) | -- (~0) | " | 0 (0.0004) | -- (~0) |
| Anthracene | " | " | 0.011 | ≤ 100 (0.1) | " | 0.032 | ≤ 100 (0.3) |
| Benzo(a)anthracene | " | " | 0.021 | " (0.2) | " | 0.058 | " (0.5) |
| Benzo(b)fluoranthene | " | " | 0.030 | " (0.2) | " | 0.060 | " (0.5) |
| Benzo(k)fluoranthene | " | " | 0.011 | " (0.1) | " | 0.026 | " (0.2) |

| Parameter | Loading Units | Sampling Periods | | | | | |
|----------------------------|--------------------|------------------|--------------|---------------|--------------------|--------------|---------------|
| | | June 20-22, 1995 | | | August 21-24, 1995 | | |
| | | Whole-Water | Particulates | %Particulates | Whole-Water | Particulates | %Particulates |
| Benzo(g,h,i)perylene | " | " | 0.021 | " (0.2) | " | 0.047 | " (0.4) |
| Benzo(a)pyrene | -- | 0 (11.794) | 0.021 | ≤ 100 (0.2) | 0 (11.794) | 0.049 | ≤ 100 (0.4) |
| Chrysene | g.d ⁻¹ | " | 0.045 | " (0.4) | " | 0.092 | " (0.8) |
| Dibenzo(a,h)anthracene | " | 0 (29.484) | 0.013 | ≤ 100 (0.04) | 0 (29.484) | 0.009 | ≤ 100 (0.03) |
| Fluoranthene | " | 0 (11.794) | 0.064 | " (0.5) | 0 (11.794) | 0.122 | " (1.0) |
| Fluorene | " | " | 0 (0.0002) | -- (~0) | " | 0 (0.0004) | -- (~0) |
| Indeno(1,2,3-cd)pyrene | " | 0 (29.484) | 0.021 | ≤ 100 (0.2) | 0 (29.484) | 0.125 | ≤ 100 (0.4) |
| Naphthalene | " | 0 (11.794) | 0.011 | " (0.1) | 0 (11.794) | 0.023 | " (0.2) |
| Phenanthrene | " | " | 0.051 | " (0.4) | " | 0.108 | " (0.9) |
| Pyrene | " | " | 0.064 | " (0.5) | " | 0.123 | " (1.0) |
| Total of 16 PAHs | " | 0 (224.) | 0.395 | " (0.2) | 0 (224.) | 0.874 | " (0.4) |
| Total PCDD/F Homologs | mg.d ⁻¹ | NS | 0.580 | ≤ 100 | NS | 0.787 | ≤ 100 |
| Total 2,3,7,8-TetraCDD TEQ | " | NS | 0.004 | " | NS | 0.01 | " |

NOTES: '--' = data not available or could not be calculated.

'0' = mean concentration below MRV.

'NS' = not sampled for this parameter.

'()' = loadings and percentages in parentheses were calculated assuming a concentration of 0.5 x MRV.

Of the persistent "trace" contaminants, inorganic and heavy metal inputs were the greatest. In this category, the highest loadings were of aluminum and strontium (from 19.0 to 10.5 kg.d⁻¹), followed by iron and barium (6.6 to 1.4 kg.d⁻¹), then by manganese, zinc, nickel, copper, cobalt, molybdenum, vanadium, chromium, titanium and lead (2.6 to 0.019 kg.d⁻¹) and lastly by arsenic, cadmium and mercury (0.003 to 0.00005 kg.d⁻¹). Aluminum is abundant in all rock types and most geologic materials (CCREM, 1987), and strontium mineral deposits are quite common in Ontario (Stephenson *et al.*, 1991a). Loadings of the major chlorinated organic contaminants, generally in the range of 0.24 to 30 grams.d⁻¹, were much lower than any of the above conventionals, inorganics and heavy metals. The greatest organics loadings were of HCBD, OCS and HCB. These compounds have lower water solubilities, but also have greater environmental persistence, partition coefficients and bioaccumulation factors than the other contaminants in this group (Howard, 1989; Mackay *et al.*, 1992a). The lack of whole-water effluent concentrations above the MRVs for PCBs and PAHs prevented a direct comparison with the loadings of other organic contaminants. However, the particulate-associated loadings of total PCBs and of individual PAH compounds (ranging from 0.009 to 0.125 g.d⁻¹) were generally one to two orders of magnitude lower than those of the chlorinated aliphatics and aromatics. As noted previously however, PAHs were not found in any whole-water effluent samples due to elevated MRVs and therefore, these particulate-derived loadings should be considered as minimal values in the overall effluent loadings evaluation. In fact, assuming a concentration of half the respective MRVs in the loadings calculations for the whole-water samples results in an estimated Total PAHs loading of 224 g.d⁻¹ (Table 4).

Effluent loadings of PCDDs and PCDFs (particulate-derived) were three orders of magnitude lower than for the above trace organics. The mean Total PCDD/F homolog loading ranged from 0.580 to 0.787 milligrams.d⁻¹. In contrast, during the 1989-90 twelve month MISA monitoring program, only one whole-water sample collected from the Cole Drain effluent contained a single

compound (i.e., OctaCDD at 50 pg.l⁻¹), which corresponds to a loading of 0.00003 mg.d⁻¹ and a Total 2,3,7,8-TetraCDD TEQ loading of 0.00000003 mg.d⁻¹. The remaining MISA effluent samples from the Cole Drain and the Polysar (now Bayer) Biox plant discharge did not contain detectable concentrations of any PCDD/F homologs or of 2,3,7,8-TetraCDD at detection limits ranging from 8 to 100 pg.l⁻¹ (Tuszynski, 1992). Loadings of the other 2,3,7,8-substituted isomers detected on 1995 Cole Drain particulates are not listed in Table 4; instead, their Toxic Equivalencies were calculated and summed (see Section 5.3.2). The mean total loading of toxic isomers expressed in terms of their potential toxicity, i.e., the Total 2,3,7,8-TetraCDD TEQ, was from 0.004 to 0.010 mg.d⁻¹, which represents 0.6 to 1.3 % of the above Total PCDD/F loadings. It is also about 5 orders of magnitude higher than the loading estimated from the 1989/90 data.

5.4.2 *Contribution of Particulates to Total Effluent Loadings*

The relative importance of particulate-associated contaminants to the total loading of contaminants from the Cole Drain effluent was parameter-dependant. For example, for most of the conventional parameters, the particulate-associated loading contributed 20 % or less of the total (whole-water) effluent loading (Table 4). Similarly, barium, cobalt, manganese, molybdenum, nickel, strontium, vanadium, and most chlorinated aliphatics and benzene compounds were mainly in the aqueous phase of the effluent. Only for phosphorus, aluminum, chromium, copper iron and zinc, did the particulate-associated loadings constitute 20 % or more of the total, with those for aluminum, chromium and iron ranging from 75 to 116 % (rounded off to 100 %). Also, due to their lack of detection in whole-water effluent samples from either survey, the loadings of arsenic, cadmium, lead, mercury, titanium and PAHs - as well as PCBs (but not the more water-soluble TriCBs and TetraCBs) during at least one of the surveys - may have been largely particulate-associated (Table 4). However, when loadings were re-calculated for these contaminants assuming their presence in the whole-water effluent at half their respective MRVs, then the particulate-associated loading contribution usually decreased to less than 20%. For PAHs, the contribution decreased to less than one percent. Chlorinated organic compounds with high organic carbon partition coefficients, such as HCBd, PentaCB, HCB and OCS, contributed a surprisingly small proportion of the total loading via particulates (i.e., from 3 to 34 %, except for OCS in the August survey, with 86 %). This is in contrast to the 1986-87 MISA Pilot Site findings, which showed that these contaminants were mainly particulate-associated in the effluent, and desorbed once the particles reached the river and were carried downstream by the current (St. Clair River MISA, 1991a & b). The 1995 results may be due to an increase in leachate infiltration from landfill(s) located within the Cole Drain system, combined with insufficient equilibration time for the adsorption of the contaminants to particulates. Such aqueous-particulate phase equilibrium partitioning may require days to occur (Jepsen & Lick, 1996).

Table 5. Estimated variability of Cole Drain effluent contaminants loadings.

| Parameter | Loading Units | Sampling Periods | | | | | | | | | | | |
|-------------------------------------|--------------------|------------------|--------|--------|--------------|-------|--------|--------------------|--------|--------|--------------|--------|--------|
| | | June 20-22, 1995 | | | | | | August 21-24, 1995 | | | | | |
| | | Whole-Water | | | Particulates | | | Whole-Water | | | Particulates | | |
| Low | Mean | High | Low | Mean | High | Low | Mean | High | Low | Mean | High | | |
| Calcium | kg.d ⁻¹ | 2039. | 3302. | 5619. | 3.59 | 9.98 | 23.4 | -- | -- | -- | 10.0 | 18.8 | 44.0 |
| Chloride | " | 1958. | 3114. | 5544. | 0.005 | 0.086 | 0.35 | 2415. | 4753. | 9515. | 0.026 | 0.052 | 0.122 |
| Carbon, dissolved Inorganic | " | 1566. | 2288. | 3709 | NS | NS | NS | 1566. | 2335. | 3896. | NS | NS | NS |
| Carbon, dissolved Organic | " | 253. | 401. | 824. | NS | NS | NS | 163. | 271. | 543. | NS | NS | NS |
| Carbon, total Organic | " | NS | NS | NS | 7.50 | 22.5 | 56.2 | NS | NS | NS | 24.5 | 48.0 | 108. |
| Loss on Ignition | " | NS | NS | NS | 16.3 | 48.8 | 122. | NS | NS | NS | 58.7 | 108. | 234. |
| Magnesium | " | 530. | 852. | 1442. | 1.55 | 4.35 | 10.3 | -- | -- | -- | 4.40 | 8.00 | 19.2 |
| Nitrogen, total Kjeldahl | " | 24.5 | 40.1 | 93.6 | 1.06 | 3.18 | 7.96 | 22.8 | 37.7 | 67.4 | 3.67 | 6.89 | 15.9 |
| Phosphorus | " | 1.63 | 4.72 | 9.36 | 0.98 | 2.55 | 5.62 | 5.71 | 10.6 | 24.3 | 3.67 | 9.29 | 15.9 |
| Potassium | " | NS | NS | NS | 0.22 | 0.61 | 1.40 | NS | NS | NS | 0.59 | 1.08 | 2.53 |
| Silicon | " | 39.2 | 56.6 | 93.6 | NS | NS | NS | 40.8 | 61.3 | 101. | NS | NS | NS |
| Sodium | " | NS | NS | NS | 0.03 | 0.08 | 0.17 | NS | NS | NS | 0.12 | 0.23 | 0.51 |
| Suspended Solids | " | 81.6 | 212. | 468. | NS | NS | NS | 245. | 436. | 936. | NS | NS | NS |
| Solvent Extractables (Oil & Grease) | " | 48.9 | 130. | 262. | 1.21 | 3.99 | 10.6 | 0 (NC) | 0 (NC) | 0 (NC) | 3.23 | 5.84 | 12.7 |
| Aluminum | g.d ⁻¹ | 4487. | 10496. | 20603. | 3018. | 7855. | 17325. | 9789. | 18988. | 43079. | 11869. | 21600. | 47761. |
| Arsenic | " | 0 (NC) | 0 (NC) | 0 (NC) | 0.579 | 1.52 | 3.37 | 0 (NC) | 0 (NC) | 0 (NC) | 1.66 | 3.08 | 6.74 |
| Barium | " | 897. | 1533. | 2809. | 6.69 | 18.8 | 44.5 | 979. | 1415. | 2248. | 21.5 | 38.9 | 85.2 |
| Cadmium | " | 0 (NC) | 0 (NC) | 0 (NC) | 0.090 | 0.287 | 0.749 | 0 (NC) | 0 (NC) | 0 (NC) | 0.563 | 1.156 | 5.385 |
| Chromium | " | 0 (NC) | 18.9 | 93.6 | 7.26 | 21.1 | 51.5 | 0 (NC) | 66.0 | 150. | 40.4 | 73.4 | 159. |
| Cobalt | " | 89.7 | 177. | 375. | 6.04 | 16.1 | 36.5 | 81.6 | 177. | 412. | 21.4 | 39.1 | 86.2 |
| Copper | " | 89.7 | 189. | 468. | 22.8 | 93.4 | 281. | 144. | 259. | 524. | 37.9 | 74.5 | 225. |
| Iron | " | 1958. | 3892. | 7117. | 1550. | 4246. | 9833. | 3263. | 6604. | 11238. | 4160. | 7636. | 17325. |
| Lead | " | 0 (NC) | 0 (NC) | 0 (NC) | 4.24 | 15.1 | 42.1 | 0 (NC) | 0 (NC) | 0 (NC) | 8.93 | 18.02 | 44.95 |
| Manganese | " | 261. | 448. | 862. | 44.9 | 121. | 276. | 367. | 2606. | 9365. | 95.4 | 178. | 412. |
| Mercury | " | 0 (NC) | 0 (NC) | 0 (NC) | 0.020 | 0.053 | 0.122 | 0 (NC) | 0 (NC) | 0 (NC) | 0.104 | 0.196 | 0.440 |
| Molybdenum | " | 64.4 | 130. | 300. | 0.196 | 0.849 | 3.090 | 97.9 | 212. | 450. | 0.832 | 1.593 | 3.886 |
| Nickel | " | 57.1 | 153. | 337. | 8.08 | 22.2 | 51.5 | 286. | 542. | 1124. | 36.7 | 66.2 | 145. |
| Strontium | " | 7260. | 11558. | 18730. | 5.30 | 13.9 | 30.9 | 8157. | 12619. | 20603. | 17.6 | 35.9 | 83.8 |
| Titanium | " | 0 (NC) | 0 (NC) | 0 (NC) | 10.6 | 28.7 | 65.6 | 0 (NC) | 0 (NC) | 0 (NC) | 26.9 | 50.9 | 112. |
| Vanadium | " | 0 (NC) | 35.4 | 137. | 2.20 | 6.16 | 14.5 | 0 (NC) | 62.5 | 187. | 5.75 | 10.7 | 24.4 |
| Zinc | " | 97.9 | 283. | 1105. | 19.6 | 56.3 | 136. | 163. | 354. | 1124. | 77.1 | 140. | 309. |
| Phenolics | " | 32.6 | 70.8 | 150. | NS | NS | NS | 0 (NC) | 212. | 1386. | NS | NS | NS |
| Hexachloroethane | g.d ⁻¹ | 0 (NC) | 0 (NC) | 1.686 | 0.0005 | 0.001 | 0.004 | 0 (NC) | 0.236 | 0.936 | 0.004 | 0.006 | 0.014 |
| Hexachlorobutadiene | " | 8.973 | 30.192 | 169. | 0.294 | 1.210 | 3.652 | 4.49 | 8.020 | 17.8 | 0.440 | 0.865 | 2.013 |
| 1,2,4-Trichlorobenzene | " | 0 (NC) | 0.826 | 5.619 | 0.001 | 0.006 | 0.017 | 0.33 | 0.708 | 1.873 | 0.007 | 0.013 | 0.028 |
| 1,3,5-Trichlorobenzene | " | 0 (NC) | 0 (NC) | 1.873 | 0.001 | 0.003 | 0.007 | 0.326 | 0.472 | 0.749 | 0.017 | 0.034 | 0.079 |
| 1,2,3,5-Tetrachlorobenzene | " | 0 (NC) | 0 (NC) | 0 (NC) | 0.002 | 0.006 | 0.015 | 0 (NC) | 0 (NC) | 0 (NC) | 0.006 | 0.012 | 0.028 |
| 1,2,4,5-Tetrachlorobenzene | " | 0 (NC) | 0 (NC) | 0 (NC) | 0.003 | 0.010 | 0.025 | 0 (NC) | 0 (NC) | 0 (NC) | 0.011 | 0.021 | 0.047 |

| Parameter | Loading Units | Sampling Periods | | | | | | | | | | | |
|----------------------------|--------------------|------------------|--------|--------|--------------|--------|--------|--------------------|--------|--------|--------------|--------|--------|
| | | June 20-22, 1995 | | | | | | August 21-24, 1995 | | | | | |
| | | Whole-Water | | | Particulates | | | Whole-Water | | | Particulates | | |
| Low | Mean | High | Low | Mean | High | Low | Mean | High | Low | Mean | High | | |
| Pentachlorobenzene | " | 0.326 | 2.241 | 22.48 | 0.016 | 0.062 | 0.178 | 0.163 | 0.354 | 0.749 | 0.028 | 0.053 | 0.131 |
| Hexachlorobenzene | g.d ⁻¹ | 0.408 | 11.558 | 142. | 0.053 | 0.334 | 1.171 | 0.408 | 0.590 | 1.311 | 0.116 | 0.199 | 0.698 |
| Octachlorostyrene | " | 0.245 | 27.244 | 337. | 0.098 | 0.860 | 3.231 | 0.163 | 0.354 | 1.124 | 0.147 | 0.303 | 0.777 |
| PCBs, total | " | 0 (NC) | 0 (NC) | 0 (NC) | 0.026 | 0.119 | 0.375 | 0 (NC) | 0 (NC) | 0 (NC) | 0.020 | 0.054 | 0.150 |
| Acenaphthene | g.d ⁻¹ | 0 (NC) | 0 (NC) | 0 (NC) | 0.003 | 0.013 | 0.037 | 0 (NC) | 0 (NC) | 0 (NC) | 0 (NC) | 0 (NC) | 0 (NC) |
| Acenaphthylene | " | " | " | " | 0 (NC) | 0 (NC) | 0 (NC) | " | " | " | 0 (NC) | 0 (NC) | 0 (NC) |
| Anthracene | " | " | " | " | 0.003 | 0.011 | 0.028 | " | " | " | 0.017 | 0.032 | 0.075 |
| Benzo(a)anthracene | " | " | " | " | 0.007 | 0.021 | 0.056 | " | " | " | 0.027 | 0.058 | 0.150 |
| Benzo(b)fluoranthene | " | " | " | " | 0.010 | 0.030 | 0.075 | " | " | " | 0.027 | 0.060 | 0.150 |
| Benzo(k)fluoranthene | " | " | " | " | 0.003 | 0.011 | 0.028 | " | " | " | 0.010 | 0.026 | 0.094 |
| Benzo(g,h,i)perylene | " | " | " | " | 0.007 | 0.021 | 0.056 | " | " | " | 0.024 | 0.047 | 0.112 |
| Benzo(a)pyrene | " | " | " | " | 0.007 | 0.021 | 0.056 | " | " | " | 0.024 | 0.049 | 0.112 |
| Chrysene | " | " | " | " | 0.015 | 0.045 | 0.112 | " | " | " | 0.044 | 0.092 | 0.225 |
| Dibenzo(a,h)anthracene | " | " | " | " | 0 (NC) | 0.013 | 0.056 | " | " | " | 0 (NC) | 0.009 | 0.112 |
| Fluoranthene | " | " | " | " | 0.018 | 0.064 | 0.178 | " | " | " | 0.054 | 0.122 | 0.337 |
| Fluorene | " | " | " | " | 0 (NC) | 0 (NC) | 0 (NC) | " | " | " | 0 (NC) | 0 (NC) | 0 (NC) |
| Indeno(1,2,3-cd)pyrene | " | " | " | " | 0.007 | 0.021 | 0.056 | " | " | " | 0.064 | 0.125 | 0.281 |
| Naphthalene | " | " | " | " | 0.003 | 0.011 | 0.028 | " | " | " | 0.012 | 0.023 | 0.056 |
| Phenanthrene | " | " | " | " | 0.016 | 0.051 | 0.131 | " | " | " | 0.051 | 0.108 | 0.262 |
| Pyrene | " | " | " | " | 0.018 | 0.064 | 0.178 | " | " | " | 0.056 | 0.123 | 0.318 |
| Total of 16 PAHs | " | 0 (NC) | 0 (NC) | 0 (NC) | 0.129 | 0.395 | 1.002 | 0 (NC) | 0 (NC) | 0 (NC) | 0.563 | 0.874 | 2.154 |
| Total PCDD/F Homologs | mg.d ⁻¹ | NS | NS | NS | 0.123 | 0.580 | 1.855 | NS | NS | NS | 0.381 | 0.787 | 1.961 |
| Total 2,3,7,8-TetraCDD TEQ | " | NS | NS | NS | 0.001 | 0.004 | 0.011 | NS | NS | NS | 0.005 | 0.01 | 0.023 |

NOTES: Loadings derived by multiplying minimum, average/mean and high concentrations by 1989-90 minimum, mean and maximum flow rates.

' - ' = no analytical result.

'NC' = could not be calculated (mean concentration below method reporting limits).

'NS' = not sampled for this parameter.

Figure 12. Cole Drain effluent whole-water and particulates contaminants loadings during June and August surveys. Vertical lines within bars represent the maximum and minimum loadings; "No Data" indicates that samples from this matrix were not submitted for analysis.

5.4.3 Contaminants Loadings Variability

Standard deviations, coefficients of variation (CVs) and confidence intervals could not be calculated for the loadings in Table 4 due to the lack of corresponding flow rates for the individual sampling dates and times. However, during the intensive monitoring of 1989-90, the CV of the final mixing chamber flow rate was 24 %, 26 % for the Cole Drain upstream of the mixing chamber, and only 12 % for the Biox Plant effluent which discharges into the mixing chamber (Tuszynski, 1992). These percentages are similar to the CVs for some of the 1995 chemical results (see Tables 2 and 3), suggesting that flow rate (particularly non-facility) may be an equally important factor in loadings calculations and loadings variability. (For example, increased flow due to high rainfall can lead to increased scouring, resuspension and transport of contaminated sediments within the system, resulting in higher final effluent loadings; alternately, it may result lower concentrations due to increased contaminant dilution.) Consequently, in addition to the mean loadings in Table 4, minimum and maximum whole-water effluent and particulates loadings were also calculated for the June and August surveys, using monthly minimum ($81\,574\text{ m}^3\cdot\text{d}^{-1}$) and maximum ($187\,300\text{ m}^3\cdot\text{d}^{-1}$) final effluent flow rates from the 1989-90 monitoring period (Tuszynski, 1992), and the minimum and maximum concentrations of the 1995 samples (see Appendices A and B). The above maximum mean flow rate is for January, 1990, when the mean flow rate of the Cole Drain upstream of the mixing chamber ($173\,570\text{ m}^3\cdot\text{d}^{-1}$) was 2.5 times that of the previous month. Over the same period, the mean monthly Biox Plant discharge increased by only 16 % (Tuszynski, 1992). This suggests the influence of non-facility inputs, such as a major rainfall event, to the system.

The June and August mean, minimum (low) and maximum (high) loadings are listed in Table 5 and the data for 22 of the parameters plotted in Figure 12. Whenever possible, these loadings have been plotted in decreasing order of magnitude, based on the total (whole-water) effluent loadings. These results show that, depending on the matrix (unfiltered effluent or particulates) and the contaminant, the minimum and maximum effluent loadings could differ by as little as two-fold (e.g., chloride in June) to 20-fold (e.g., HCBd in June) or more (e.g., phenolics in August). In view of the absence of rain during or immediately prior to the two sampling periods, these loadings probably represent a conservative estimate.

5.4.4 Coal Drain Effluent Loading Trends and Relative Contribution to the River

Table 6 compares the 1995 overall average Cole Drain contaminant loadings with the results from earlier studies in 1989-90, 1986-87, 1986, 1985 and 1984-85. It also provides a comparison with gross and net daily loadings to the St. Clair River from Lake Huron and from the lower St. Clair River to Lake St. Clair during the periods 1987-89 and 1984-85. The latter information was derived from samples collected at Point Edward and near Port Lambton or within in the South Channel, respectively. (The 1995 loadings for the lower St. Clair River were unavailable at the time of report writing.) Use of these data for statistical trend analysis presents some difficulties, mainly due to the: lack of study-to-study comparability of analytical parameter lists; differences in sampling times and study duration, sampling protocol and the flow rate used in the

Table 6. Comparison of present (1995) and historical Cole Drain and Dow Scott Rd. Landfill effluent loadings and limits with St. Clair River contaminants loadings. Note differences in loadings calculations (gross vs. net).

| Parameter | Units | Scott Rd. Landfill | Cole Drain | | | | | | | upper SCR | lower St. Clair River | | |
|-------------------------------------|---------------------------------|--|---|-------------------------------------|------------------------------------|---|----------------------------|---------------------------------|--|-------------------------------|-------------------------------|---|--|
| | | Daily / Monthly Average Loading Limit (EPA Reg. 6/95, Schedule 2) | Recommended Monthly Mean Load Allocation. (St. Clair R. MISA, 1991a) | 1995 gross (this study; average) | 1989-90 gross (Tuszynski, 1992) | 1986-87 net (St. Clair R. MISA, 1991a,b) | 1986 net (UGLCCS, 1989) | 1985 gross (EC & OMOE, 1986) | 1984-85 gross (Johnson & Kauss, 1991) | 1987-89 gross (Chan, 1993) | 1987-89 gross (Chan, 1993) | 1987-89 net (within-river additions) (Chan, 1993) | 1984-85 gross (Johnson & Kauss, 1987) |
| Flow Rate | m ³ .d ⁻¹ | -- | -- | 117937 | 117937. | 135240. | 147000. | 140000. | 71740. | 4428333300 | 4606976700 | 178643400 | 550022400 |
| Calcium | kg.d ⁻¹ | -- | -- | 3302. | -- | -- | -- | -- | -- | 12267000 | 12303000. | 36000 | -- |
| Carbon, Dissolved Inorganic | " | -- | -- | 2312. | -- | -- | -- | -- | 1821. | -- | -- | -- | -- |
| Carbon, Dissolved Organic | " | 27. / 6.1 | -- | 336. | 510. | -- | -- | -- | 426. | -- | -- | -- | -- |
| Carbon, Total Organic | " | -- | -- | ≥35.3 | 608. | -- | -- | -- | -- | -- | -- | -- | -- |
| Chloride | " | -- | -- | 3934. | -- | 7818. | 11400. | -- | 5381. | 2657000 | 3962000. | 1305000 | 4200000. |
| Magnesium | " | -- | -- | 852. | -- | -- | -- | -- | -- | 3212000 | 3237000. | 25000 | -- |
| Nitrogen, total Kjeldahl | " | 1.7 / 0.62 | -- | 38.9 | 54.4 | -- | -- | -- | 149. | 62100 | 74500. | 12400 | -- |
| Phosphorus, total | " | 0.14 / 0.053 | -- | 12.1 | 17.8 | -- | -- | -- | 6.35 | 1800 | 2200. | 400 | 5500. |
| Solvent Extractables (Oil & Grease) | " | 1.8 / 1.4 | -- | 65. | 206. | -- | 1300. | -- | -- | -- | -- | -- | -- |
| Suspended Solids | " | 2.6 / 1.3 | -- | 324. | 898. | 3061. | 3061. | -- | 1637. | 1568886 | 1586304 | 17418 | 5000000. |
| Aluminum | g.d ⁻¹ | 22. / -- | -- | 14742. | 29770. | -- | -- | -- | 22810. | 20857450 | 69887837 | 49030387 | -- |
| Arsenic | " | -- | -- | ≥2.30 | -- | -- | -- | -- | 70.0 | -- | -- | -- | -- |
| Barium | " | -- | -- | 1474. | -- | -- | -- | -- | -- | 5756833 | 8661116 | 2904283 | -- |
| Cadmium | " | -- | -- | ≥0.724 | -- | 46.5 | 46.5 | -- | 31.1 | 17713 | 32249 | 14536 | -- |
| Cobalt | " | -- | -- | 177. | 253. | -- | -- | -- | 77.8 | 17713 | 87533 | 69820 | -- |
| Chromium | " | -- | -- | ≥47.3 | -- | -- | 8.92 | -- | 210. | 137278 | 299453 | 162175 | -- |
| Copper | " | -- | -- | 224. | -- | -- | 1320. | -- | 1166. | 433977 | 806221 | 372244 | -- |
| Cyanide | " | -- | -- | 0 (NC) | -- | -- | 539. | -- | -- | -- | -- | -- | -- |
| Iron | " | -- | -- | 5248. | -- | -- | 23500. | -- | 41904. | 23470167 | 137794674 | 114324507 | 76000000. |
| Lead | " | -- | -- | ≥16.7 | -- | 385. | -- | -- | 210. | 39855 | 391593 | 351738 | 16000000 |
| Manganese | " | -- | -- | 1527. | -- | -- | -- | -- | 510. | 695248 | 5150600 | 4455352 | -- |
| Mercury | " | 0.042 / -- | 2.2 | ≥0.125 | -- | 2.2 | -- | -- | 1.64 | -- | -- | -- | 6600 |
| Molybdenum | " | -- | -- | 171. | 461. | -- | -- | -- | -- | -- | -- | -- | -- |
| Nickel | " | -- | -- | 348 | 1123. | -- | 243. | -- | 358. | 252415 | 446877 | 194462 | -- |
| Strontium | " | -- | -- | 12089. | -- | -- | -- | -- | -- | 43131967 | 60535674 | 17403707 | -- |
| Vanadium | " | -- | -- | 49.0 | -- | -- | -- | -- | -- | 101852 | 230349 | 128497 | -- |
| Zinc | " | -- | -- | 319 | 987. | -- | 2000. | -- | 1065. | 132850 | 847684 | 714834 | 1100000 |

| Parameter | Units | Scott Rd. Landfill | Cole Drain | | | | | | | upper SCR | lower St. Clair River | | |
|--------------------------|--------------------|--|---|-------------------------------------|------------------------------------|---|----------------------------|---------------------------------|---|-------------------------------|-------------------------------|---|---|
| | | Daily / Monthly Average Loading Limit (EPA Reg. 6/95, Schedule 2) | Recommended Monthly Mean Load Allocation. (St. Clair R. MISA, 1991a) | 1995 gross (this study; average) | 1989-90 gross (Tuszynski, 1992) | 1986-87 net (St. Clair R. MISA, 1991a,b) | 1986 net (UGLCCS, 1989) | 1985 gross (EC & OMOE, 1986) | 1984-85 gross (Johnson & Kaus, 1991) | 1987-89 gross (Chan, 1993) | 1987-89 gross (Chan, 1993) | 1987-89 net (within-river additions) (Chan, 1993) | 1984-85 gross (Johnson & Kaus, 1987) |
| Phenolics | g.d ⁻¹ | 6.2 / 2.3 | -- | 141 | 330. | -- | 880. | -- | 1423. | -- | -- | -- | -- |
| Hexachloroethane | g.d ⁻¹ | 0.28 / 0.20 | 6.8 | ≥0.118 | 1 | 6.81 | -- | 57.4 | 5.33 | -- | -- | -- | -- |
| Hexachlorobutadiene | " | 0.28 / 0.20 | 87 | 19.1 | 7 | 140 | -- | 210 | 5.09 | >0 (ND) | >185.6 | ~185.6 | -- |
| 1,2,3-Trichlorobenzene | " | -- | -- | 0 (NC) | -- | 13.9 | -- | 1.15 | -- | -- | -- | -- | -- |
| 1,2,4-Trichlorobenzene | " | 3.0 / 1.1 | -- | 0.767 | 1 | 1.89 | -- | 322 | -- | >38 | >29. | -9 | -- |
| 1,3,5-Trichlorobenzene | " | -- | -- | 0.236 | -- | 1.04 | -- | 23.8 | -- | >0 (ND) | >7. | ~7. | -- |
| 2,3,6-Trichlorotoluene | " | -- | -- | 0 (NC) | -- | 0.03 | -- | -- | -- | -- | -- | -- | -- |
| 2,4,5-Trichlorotoluene | " | 0.43 / 0.20 | 9.6 | 0 (NC) | 10. | 9.54 | -- | -- | -- | -- | -- | -- | -- |
| 2,6,a-Trichlorotoluene | " | -- | -- | 0 (NC) | -- | 0.05 | -- | -- | -- | -- | -- | -- | -- |
| 1,2,3,4-Trichlorobenzene | " | -- | -- | 0 (NC) | -- | 0.62 | -- | 1.4 | -- | -- | -- | -- | -- |
| 1,2,3,5-Trichlorobenzene | " | -- | -- | ≥0.009 | -- | 0.58 | -- | 2.8 | -- | -- | -- | -- | -- |
| 1,2,4,5-Trichlorobenzene | " | -- | -- | ≥0.016 | -- | 0.85 | -- | 1.05 | -- | -- | -- | -- | -- |
| Pentachlorobenzene | " | -- | -- | 1.30 | 1. | 9.1 | -- | 3.22 | -- | >6. | >7.8 | ~1.8 | -- |
| Hexachlorobenzene | " | 0.10 / -- | 3.9 | 6.07 | 2. | 8.88 | 0.5 | 2.52 | 4.32 | >9. | >17.6 | ~8.6 | 800. |
| Octachlorostyrene | " | 0.21 / 0.20 | 0.015 | 13.8 | 1. | 9.16 | -- | 0.59 | 1.71 | ≥0 (ND) | ≥33.6 | ~33.6 | 200. |
| PCBs, total | " | -- | -- | ≥0.087 | -- | -- | 0 (NC) | 0 (NC) | ≥0.345 | >536 | >755. | ~219. | 300 |
| Total of 16 PAHs | g.d ⁻¹ | -- | -- | ≥0.635 | -- | -- | 172. | 27.76 | -- | -- | -- | -- | -- |
| Total PCDD/F Homologs | mg.d ⁻¹ | -- | -- | ≥0.683 | 0 | -- | -- | -- | -- | -- | -- | -- | -- |
| Total 2,3,7,8-TCDD TEQ | " | monitor | -- | ≥0.007 | 0 | -- | -- | -- | -- | -- | -- | -- | -- |

NOTES: 'NC' = could not be calculated (mean concentration below minimum reportable value); loading assumed to be zero.

'--' = no data available for this parameter.

'>' = loading is a minimum, based only on detection in the particulate (suspended sediment) fraction.

'>' = loading is a minimum, based only on detection in the aqueous (particulates removed) fraction.

'<' = loading is maximum, based on detection in one sample.

'~' = approximately.

1989/90 (Tuszynski, 1992) loadings are the sum of Biox plant and Cole Drain loadings (latter was monitored upstream of mixing chamber).

loadings calculations - in some cases “gross”, in others “net”. Therefore, the following discussion is comparative and based on averages or means. Note however, that comparison of the 1995 Cole Drain inputs with the average of the 1987 through 1989 lower river loadings (higher than present loadings, but the most recent available) very likely underestimates the relative importance or percentage contribution of this discharge to the St. Clair River.

Overall, for the non-organic contaminants listed in Table 6, the 1995 Cole Drain discharge loadings appear to constitute only a small fraction of the 1987-1989 daily Lake Huron input to the St Clair River (ranging from 0.004 % for cadmium, to 1 % for cobalt) or of the gross lower St. Clair River output (ranging from 0.004 % for iron and lead, to 0.5 % for phosphorus). When compared to the net lower St. Clair river loadings (i.e., gross output minus gross input) for this period, the Cole Drain contribution increases slightly, from a minimum of 0.005 % for iron and lead to a maximum of 3.4 % for magnesium.

Furthermore, loadings of some contaminants from the Cole Drain discharge appear to have been decreasing over the years. These include chloride, total Kjeldahl nitrogen, oil and grease, suspended solids, aluminum, copper, iron, molybdenum, zinc, phenolics, HCE, HCB, 1,2,4,-TriCB and 1,3,5-TriCB. Inputs of some of these contaminants seem to have decreased appreciably after the mid-1980s. In fact, the mean HCE and HCB loadings in 1995 were below their respective recommended monthly mean load allocations of 6.8 g.d⁻¹ and 87 g.d⁻¹, respectively (St. Clair River MISA, 1991a). (These load allocations, or limits, were recommended by the 1986-87 St. Clair River MISA Pilot Site Study of the Organic Chemical Sector, based on extensive sampling of effluents, river water and aquatic biota. They were determined by modelling the impact of effluent loadings and selected to provide compliance with receiving water quality objectives 95 % of the time. However, since the twice-weekly 1986-87 effluent sampling occurred during both dry and wet weather events, the HCE and HCB loadings decreases may not be as great as a comparison of the means would initially indicate.) A decreasing trend through time was also evident in the concentrations of some contaminants measured by the long-term, year-round head and mouth monitoring of the St. Clair River by Environment Canada. For example, there were statistically significant decreases between 1988 and 1989 in the concentrations of 1,3,5-TriCB, HCB, PentaCB, HCB and OCS on suspended sediment samples collected in the lower river at Port Lambton (Chan, 1993). Furthermore, over the period 1990 through 1995, there was a large decrease in the aqueous phase (i.e., particulates removed) chloride concentration at Port Lambton. Similarly, the aqueous phase HCB concentration and particulate-associated concentrations of 1,3,5-TriCB, HCB, PentaCB, HCB and OCS at Port Lambton have exhibited a steady decline since 1988, although their levels are still noticeably higher in summer samples (Chan & Harrison, 1997). (This summer phenomenon may be related to shipping-induced resuspension of contaminated sediments along the Bayer-Dow shoreline (McCorquodale & Tomczak, 1998).) The largest decreases in most of these contaminants occurred during the 1988-91 period, with concentrations having levelled off since then.

Nevertheless, the loadings data in Table 6 do indicate that the Cole Drain has been and (as of 1995) continues to be an important source of a number of the above chlorinated organic

contaminants to the St. Clair River - particularly of HCB, PentaCB, HCB and OCS, the more persistent and bioaccumulative chlorinated aliphatic and aromatics (Mackay *et al.*, 1992a; Howard, 1989; Oliver & Niimi, 1983). The 1995 Cole Drain loadings ranged from 2 % for 1,2,4-TriCB to 67 % for HCB of the 1987-1989 Lake Huron input loadings to the river, and from 3 % for 1,2,4-TriCB to 41 % for OCS, of the gross 1987-89 lower river loadings. When compared to the net lower river loadings, the contribution from the drain is substantially greater for some of these compounds, e.g., 71 % for HCB and 72 % for HCB. Given the potentially large variation in contaminant concentrations and loadings from the Cole Drain (see Section 5.4.3), this contribution could vary greatly - e.g., for HCB, averaging 10 % of the lower river load, but potentially ranging from as little as 2 % to as much as 91 %. It should be noted however, that the contribution of the Cole Drain input to the contaminant load carried by the lower river was probably even greater for 1995, since the above percentages are based on a comparison with 1987-89 lower river data, when concentrations and loadings of HCB, HCB and OCS were two to three times higher than in 1995 (Chan & Harrison, 1997).

The 1995 daily average Coal Drain loadings of HCB and OCS were still 1.5 and 920 times their St. Clair River MISA (1991a) Recommended Mean Monthly Load Allocations of 3.9 and 0.015 g.d⁻¹, respectively (see Table 6). Through the St. Clair River RAP Stage 2 process, the Cole Drain was identified as a priority source of HCB, PentaCB, HCB and OCS (Geomatix, 1997). On February 16, 1998, Environmental Protection Act daily loading limits for contaminants permitted into the Cole Drain from the Scott Road Landfill wastewater treatment system (see Table 6) became effective. Since the Scott Road Landfill has been a major source of a number of contaminants - particularly chlorinated aliphatics and aromatics - these limits, if met, should assist greatly in reducing inputs from the Cole Drain to the St. Clair River.

No PCDD and PCDF concentration or loadings data for the lower St. Clair River were available for comparison with the 1995 Cole Drain data. The little historical information available for the Cole Drain discharge shows that the average 1995 Total PCDD/F loading (based only on particulates data) was over 20000 times greater than that calculated from the 1989-90 MISA whole-water monitoring data (Table 6). Additional samples, collected as part of a routine monitoring program, are required to better quantify the loadings of this highly toxic and persistent group of contaminants.

5.4.5 Possible Sources of Contaminants to the Cole Drain

Appendix C summarizes the industrial, municipal and commercial uses of the persistent contaminants that were found at higher concentrations in Cole Drain effluent samples than in upstream Lake Huron samples collected at Point Edward. These uses relate to the specific industrial (petroleum and organic chemical) and municipal dischargers, stormwater and site runoff sources identified in Section 1. It should, however, be noted that the detection of certain contaminants in the Cole Drain system may be related to historical manufacturing practices. For example, the manufacture of chlorine-based hydrocarbons by Dow Chemical ceased in 1993, and

Figure 13. Cole Drain effluent whole-water, effluent particulates and sediment organic contaminant profiles. Compounds are listed in order of decreasing water solubility, and increasing organic carbon partition coefficient and bioaccumulation factor, from left to right. Note differences in concentration units (ppt vs. ppm) between the different matrices.

this should also have had an impact on the generation of waste by-products such as HCBd, HCB and OCS. Although insufficient river data were available to assess the importance of Cole Drain loadings of PAHs, PCDDs and PCDFs, potential sources of these contaminants are also listed in Appendix C, since they are persistent and bioaccumulative and are on the Contaminants of Concern list for the St. Clair River (St. Clair River RAP, 1995). It is noteworthy that chlorinated aliphatics and aromatics are often organic chemical process intermediates, impurities or waste by-products. Also, many heavy metal compounds are utilized as catalysts, stabilizers or additives by both the organic chemical and the petroleum industries, and are important in numerous other processes or products (Appendix C).

Some of the chlorinated organic wastes, as well as others, have been disposed of in landfills situated along the Cole Drain-Scott Road Ditch system. In 1985, a number of the chlorinated aliphatic and aromatic compounds, as well as volatile solvents, were present in Scott Road Ditch effluent samples, even after carbon treatment (EC & OMOE, 1986). The PCDDs and PCDFs found at ppt levels in the 1995 Cole Drain effluent particulates may also have originated from a landfill. In 1985, sediment from the drain contained $0.17 \mu\text{g}\cdot\text{kg}^{-1}$ (ppb) HeptaCDD and $0.44 \mu\text{g}\cdot\text{kg}^{-1}$ OctaCDD, as well as concentrations of tri-, tetra- and pentachlorophenols ranging from 0.25 to $1.3 \mu\text{g}\cdot\text{kg}^{-1}$. Chlorophenols, 2,4-D, 2,4,5-T and PAH compounds were found in the Dow Scott Road landfill leachate in 1985 and the Scott Road outfall contained many of the contaminants discharged by the landfill, albeit at lower concentrations (EC & OMOE, 1986).

Their detection in the Cole Drain discharge suggests that a number of the above-noted chlorinated organic contaminants probably originated either directly from landfills, or indirectly through the resuspension of contaminated sediments still located within the system. (Monitoring during 1989-90 (Tuszynski, 1992) showed that the Biox Plant effluent contributed under half of the final Cole Drain discharge loading of most contaminants, particularly for the chlorinated aliphatics and aromatics.) With regard to resuspension, the concentration pattern of selected chlorinated aliphatics and aromatics in sediment collected in December 1995 near Kenney Street (Kauss, 1996) is illustrated in Figure 13. A sediment sample obtained from the Cole Drain at the bridge leading to the (then) ArmaK Chemicals building in 1985 (EC & OMOE, 1986) exhibited a very similar contaminant profile (Fig. 13). Although concentrations in both samples were in the ppm range, levels in the 1995 sample were about an order of magnitude higher than in 1985. Whether this is due to differences in sampling locations, analytical methods or increased contamination over the years is unknown. Concentrations of these contaminants in the 1995 effluent particulates were about one to two orders of magnitude lower than in the sediments. Comparing the average concentrations of chlorinated aliphatic and aromatic contaminants in the whole-water effluent with levels found in effluent particulates indicates a similar pattern to that observed in the two sediment samples, again with HCBd and OCS dominating the profile (Fig. 13). These data suggest that historically contaminated sediments within the Cole Drain system may well be eroding and contributing to the final effluent loading of particulate-associated chlorinated organics. The lower contaminant concentrations found in effluent particulates than in sediments may be due to dilution by cleaner particles originating elsewhere (i.e., further upstream) in the Cole Drain system.

Table 7. Cole Drain, Scott Road Ditch and St. Clair River contaminants concentrations, November 22-23, 1995.
 All concentrations in ng.l⁻¹ (ppt). Source: G. Szober, OMOE Sarnia District Office. See Figure 2 for sampling locations.

| Parameter | Sampling Location & Number | | | | | | | | | | | | | |
|--------------------------------|---|--|----------------------------|---|-----------------------------|------------------------------------|--------------------------------|-----------------------------|--------------------------------------|-------------------------------------|--|--------------|----------------------------------|----------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | | | |
| | Cole Drain, upstream of Scott Road - effluent | Flyash Pond Drain perimeter ditch - effluent | Scott Rd. Drain - effluent | Cole Drain, downstream of Scott Road bridge | Bayer Biox plant - effluent | Cole Drain, at Vidal Street bridge | Scott Rd. Drain, culvert inlet | Cole Drain - final effluent | St. Clair River, upstream of outfall | St. Clair River, in discharge plume | St. Clair River, downstream of outfall | Travel Blank | St. Clair RAP Environ. Yardstick | PWQ / IPWQ Objective |
| Flow Rate, l.min ⁻¹ | 9.63 | -- | -- | 70.3 | -- | 137.3 | -- | 1 596. * | -- | -- | -- | -- | -- | -- |
| Trichloroethane | nd | 27 000 | 25 000 | 4 000<T | nd | 2 000<T | nd | nd | nd | nd | nd | nd | 120 000 | 10 000 |
| Tetrachloroethene ("Perc") | nd | 19 000 | 33 000 | 5 000 | nd | 1 000<T | nd | nd | nd | nd | nd | nd | 8 000 | 50 000 |
| 1,1,2-Trichloroethane | nd | 65 000 | 11 000 | nd | nd | 3 000<T | nd | nd | nd | nd | nd | nd | 27 000 | 800 000 |
| Hexachloroethane | 30 | 13 000 | 11 000 | 1 100 | 1<W | 1 500 | 1<W | 75 | 7<T | 59 | 27 | 2<T | 13000 | 1000 |
| Hexachlorobutadiene | 45 | 12 000 | 55 000 | 5 800 | 15 | 10 000 | 10 | <u>550</u> | 7<T | <u>400</u> | <u>140</u> | 1<W | 100 | 9 |
| 1,2,3-Trichlorobenzene | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | -- | 900 |
| 1,2,4-Trichlorobenzene | 4<T | 430 | 37 000 | 3 300 | 110 | 4 500 | 2<W | 240 | 2<W | 165 | 60 | 2<W | -- | 500 |
| 1,3,5-Trichlorobenzene | 2<W | 190 | 6 000 | 700 | 2<W | 1 500 | 2<W | 90 | 2<W | 67 | 26 | 2<W | -- | 650 |
| 2,3,6 -Trichlorotoluene | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | -- | -- |
| 2,4,5 -Trichlorotoluene | 1<W | 510 | 42 000 | 4700 | 1<W | 5 800 | 1<W | 380 | 1<W | 270 | 88 | 1<W | -- | -- |
| a,2,6 -Trichlorotoluene | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | -- | -- |
| 1,2,3,4-Tetrachlorobenzene | 1<W | 1<W | 1<W | 1<W | 1<W | 80 | 1<W | 1<W | 1<W | 1<W | 1<W | 1<W | -- | 100 |
| 1,2,3,5-Tetrachlorobenzene | 1<W | 410 | 870 | 140 | 1<W | 150 | 1<W | 30 | 1<W | 10 | 5<T | 1<W | -- | 100 |
| 1,2,4,5-Tetrachlorobenzene | 1<W | 55 | 500 | 75 | 1<W | 75 | 1<W | 10 | 1<W | 1<W | 5<T | 1<W | -- | 150 |
| Pentachlorobenzene | 1<W | 110 | 3 900 | 510 | 1<W | 540 | 1<W | <u>45</u> | 1<W | <u>40</u> | 20 | 1<W | 30 | 30 |
| Hexachlorobenzene | 1<W | 45 | 1 200 | 280 | 2<T | 180 | 1<W | <u>15</u> | <u>7<T</u> | <u>30</u> | <u>7<T</u> | 1<W | 1 | 6.5 |
| Octachlorostyrene | 1<W | 40 | 1 900 | 420 | 1<W | 180 | 1<W | 14 | 1<W | 22 | 6<T | 1<W | -- | -- |

NOTE: underline value in shaded cell exceeds Environmental Yardstick (St. Clair River RAP, 1995) and Provincial Water Quality Objective(OMOE, 1994a).

* flow rate (\cong to 137,940 m³.day⁻¹) was calculated from mean of concentration dilution factors between stations 6 and 7.

"nd" = not detected.

Figure 14. **Organic contaminant profiles of November 22-23, 1995 Cole Drain and Scott Road Ditch samples.** Sample locations are ordered from upstream (left) to downstream (right) in the drain system. Contaminants are listed in order of decreasing water solubility, and increasing organic carbon partition coefficient and bioaccumulation factor, bottom to top.

were found in the Cole Drain waters at least as far downstream as the Vidal Street Bridge. These concentrations are similar to those in samples collected in 1980 and 1981 (see Appendix D) and in 1985 (EC & OMOE, 1986). Apart from the much higher concentration of HCE in the Flyash Pond Drain sample, the contaminant profile was similar in samples obtained from within the Cole Drain (see Fig. 14). As shown previously (Fig. 13), HCBd was the dominant chlorinated aliphatic/aromatic contaminant in all samples. The absence of 2,4,5-trichlorotoluene in the June and August effluent and particulate samples, but presence in the late November samples, may be due to temperature-dependant hydrolysis. Such abiotic degradation occurs ten times more rapidly at 25°C than at 5.1°C with benzotrchlorides, a similar group of compounds (Howard, 1989).

Table 7 also shows that, at the time of sampling, some of the persistent organics concentrations in the final effluent exceeded the Provincial Water Quality Objectives or Interim Water Quality Objectives for the Protection of Aquatic Life (OMOE, 1994a) by factors of 61 for HCBd, 1.5 for PentaCB and 2.3 for HCB. They also exceeded the St. Clair River Environmental Water Quality Yardsticks (St. Clair River RAP, 1995) by factors ranging from 5.5 for HCBd to 15 for HCB. Within the discharge plume in the St. Clair River as well as somewhat further downstream, the PWQOs/IPWQOs were exceeded by factors of 44 and 15 for HCBd, 1.3 for PentaCB, and 4.6 and 1.1 for HCB.

During the June and August 1995 surveys, the final effluent concentrations also exceeded the PWQOs, IPWQOs or RAP Yardsticks for phosphorus, aluminum, cobalt, HCBd and HCB in a majority of the samples from both surveys, usually by about two-fold, but up to 100-fold for HCBd and 760-fold for HCB (Table 8). Although OCS was also present in the effluent, no objective or yardstick is currently available for this compound.

Table 8. Cole Drain effluent concentrations relative to aquatic life objectives.

| Parameter | Aquatic Life Objectives | | Percent of Samples Exceeding ** | | | Factor Exceeded by ** | | |
|------------|----------------------------|--------------------------|---------------------------------|----------|-----------|-----------------------|-----------|-----------|
| | PWQO/IPWQO * | Yardstick | Overall | Minimum | Maximum | Overall | Minimum | Maximum |
| Phosphorus | 0.030 mg.l ⁻¹ * | 0.020 mg.l ⁻¹ | 83 / 89 *** | 67 / 77 | 100 / 100 | 2.2 / 3.2 | 1.3 / 1.5 | 4.3 / 6.5 |
| Phenolics | 0.001 mg.l ⁻¹ | -- | 22 | 0 | 44 | 3.5 | 1.6 | 7.4 |
| Aluminum | 75 µg.l ⁻¹ | -- | 94 | 89 | 100 | 1.7 | 1.03 | 3.1 |
| Cadmium | 0.2 µg.l ⁻¹ | 0.5 µg.l ⁻¹ | 17 / 0 | 0 / 0 | 22 / 0 | 1.2 / 0 | 1.05 / 0 | 1.3 / 0 |
| Cobalt | 0.9 µg.l ⁻¹ * | -- | 100 | 100 | 100 | 2.5 | 1.7 | 3.7 |
| HCBd | 9 ng.l ⁻¹ * | 100 ng.l ⁻¹ | 100 / 50 | 100 / 0 | 100 / 100 | 18 / 1.6 | 6.1 / 1.1 | 100 / 9.0 |
| HCB | 6.5 ng.l ⁻¹ | 1 ng.l ⁻¹ | 28 / 100 | 11 / 100 | 44 / 100 | 26 / 51 | 1.1 / 5.0 | 117 / 760 |

NOTE: "***" = overall results for June and August, 1995 surveys, and minimum & maximum from the two surveys.
 "****" = parameters with two percents or factors are for PWQO/IPWQO & Yardstick, respectively.
 "--" = not available.

6.0 CONCLUSIONS AND RECOMMENDATIONS

- (i) The largest contaminant loadings from the Cole Drain to the St. Clair River are of “conventionals” such as chloride, calcium, dissolved inorganic and organic carbon, magnesium, suspended solids, solvent extractables, total Kjeldahl nitrogen, total phosphorus and silicon (tonnes to kilograms per day). Inputs of heavy metals and chlorinated organic contaminants represented a much smaller daily loading to the St. Clair River (in kilograms, grams, or milligrams per day). Nevertheless, many of these compounds, such as certain heavy metals, HCB, HCB, OCS, PCBs, PAHs, and PCDDs and PCDFs are both persistent and bio-accumulative. The fact that the major loading of some of these metals and chlorinated aliphatics and aromatics is mainly aqueous rather than particulate-associated suggests that water-solids equilibrium partitioning had not yet been achieved in the discharge and that, as a result, these contaminants may be more readily available for accumulation by aquatic biota immediately after their discharge to the river.

Higher mean whole-water effluent and/or particulate contaminant concentrations in the Cole Drain than in upstream Point Edward (Lake Huron) water or particulates indicate that the discharge is a potentially important source of (at least) chloride, dissolved organic carbon, total Kjeldahl nitrogen, total phosphorus, aluminum, cobalt, copper, iron, manganese, molybdenum, nickel, vanadium, zinc, hexachloroethane, HCB, 1,2,4,-trichlorobenzene (TriCB), 1,3,5-TriCB, PentaCB, HCB, OCS, fluoranthene, phenanthrene, pyrene, and total PCBs to the St. Clair River ecosystem. Of these parameters, chloride, total Kjeldahl nitrogen, total phosphorus, copper, manganese, nickel, zinc, HCB, OCS, PCBs and PAHs have been identified as “Chemicals of Concern” by the St. Clair River Remedial Action Plan. Also on this list are the PCDDs and PCDFs, which were detected in all of the particulates samples.

Inputs of some contaminants appear to have decreased appreciably after the mid-1980s. These include chloride, total Kjeldahl nitrogen, oil and grease, suspended solids, aluminum, copper, iron, molybdenum, zinc, phenolics, HCE, HCB, 1,2,4,-TriCB and 1,3,5-TriCB. (This decrease may also be related to weather conditions during the effluent sampling) For example, the average HCE and HCB loadings during the 1995 surveys were below their respective receiving-water-based load allocations designed to provide compliance with water quality objectives 95 % of the time. However, when compared to the total load carried by the lower St. Clair River, it is evident that the Cole Drain has been and continues (as of 1995) to be an important source of a number of persistent organic contaminants to the river ecosystem, particularly of HCB, PentaCB, HCB and OCS, the more persistent and bioaccumulative chlorinated aliphatic and aromatics. In fact, the mean 1995 Coal Drain loadings of HCB, and particularly OCS, were still above their recommended load allocations, designed to achieve 95 % compliance with water quality objectives, and concentrations of HCB, PentaCB and HCB within the effluent discharge plume (and of HCB and HCB downstream of the discharge) exceeded either

their St. Clair River Environmental Water Quality Yardsticks, or the Provincial Guidelines for the Protection of Aquatic Life.

Recommendation: Monitoring of current effluent conditions, subsequent to the Dow remediation project in 1997, is necessary to further delineate changes in contaminant concentrations and loadings to the St. Clair River. Any monitoring program for the Cole Drain final mixing chamber effluent should include, in addition to conventional parameters, the above-noted persistent heavy metals (aluminum, cobalt, copper, iron, manganese, molybdenum, nickel, vanadium, zinc) and organics (chlorinated benzenes and aliphatics, PCBs, PAHs, PCDDs and PCDFs). This should verify what, if any, further reductions are needed as a result of recent remediation efforts by Dow Chemical on the Cole Drain/Scott Road Ditch system.

- (ii) All of the conventional parameters monitored, including calcium, chloride, magnesium, nutrients, the dissolved carbons, suspended solids, as well as a number of the inorganics and heavy metals were present in all Cole Drain whole-water effluent samples. Also, certain chlorinated aliphatics and aromatic contaminants identified as chemical intermediates or waste by-products of chlorinated solvents production were consistently found in the effluent. These included: HCB, PentaCB, HCB and OCS. No mercury or PAH compounds were detected in the whole-water effluent samples, due in the latter case, to the high analytical detection limits for PAH compounds and the (presumed) low effluent concentrations.

The collection and analysis of effluent particulates considerably enhanced the detection of trace contaminants. These effluent particulates were primarily in the fine sand to very fine clay size range, with medium to coarse silt in greatest abundance. Such particles have a high surface-to-volume ratio, which, in combination with their relatively high organic carbon content, provides a suitable site for the adsorption of contaminants with low water solubility and high particulate- and organic carbon partition coefficients. Consequently, additional inorganics and heavy metals, many chlorinated aliphatics and aromatics, PCBs, and most PAHs, PCDD and PCDF homolog groups and their toxic (2,3,7,8-substituted) isomers were detected in the particulates samples.

The relative contribution of particulate-associated contaminants to the total loading of contaminants from the Cole Drain effluent was parameter-dependant. For most of the conventional parameters, the particulate-associated loading contributed 20 % or less of the total (whole-water) effluent loading. Only the particulate-associated loadings of phosphorus, aluminum, chromium, copper iron and zinc constituted 20 % or more of the total loading, with those for aluminum, chromium and iron ranging from 75 % to 100%. Chlorinated organic compounds with high organic carbon partition coefficients, such as HCB and OCS, contributed a surprisingly small proportion of the total loading via particulates, i.e., as much as 86 % for OCS in the August survey, but usually less than 35%. This may have been due to insufficient equilibration time between the aqueous and particulate phases.

Recommendation: Analysis of centrifuged (or filtered) particulates may be one of the few effective means of detecting and adequately quantifying contaminants which are present at low concentrations and exhibit a high degree of partitioning onto particulates. However, if there is a need to acquire data on the total (whole-water) effluent loadings for these contaminants, then lower analytical detection limits and/or larger sample volumes will need to be employed. In view of anticipated reductions in contaminant concentrations following remedial action by Dow, centrifugation and/or large volume sampling will be necessary to quantify the impact of these changes.

- (iii) Estimations of the variability in contaminants loadings using the minima and maxima of the survey concentrations and of historical flow data indicated that, depending on the contaminant and the matrix sampled (i.e., unfiltered effluent vs. particulates), the minimum and maximum loadings could differ by as little as two-fold to greater than 20-fold. This appears to be related to a high degree of short-term temporal variability (i.e., within a matter of hours) in the concentrations of certain contaminants. Furthermore, given the number of potential storm water inputs to the Cole Drain, high rainfall events may affect these loadings considerably.

Recommendation: Concurrent with any Cole Drain final effluent sampling, flow monitoring of the final mixing chamber effluent is necessary to provide more accurate loadings calculations. Also, to reduce variability and improve loadings estimates, 24-hour composite sampling over a number of randomly-selected days is recommended; this should include wet weather events and (ideally) flow-weighted sampling.

- (iv) Comparison of the 1995 results to those of earlier studies indicates the continuing presence in the Cole Drain final (whole-water) effluent and/or in effluent particulates of: a number of chlorinated aliphatics and aromatics (dominated by HCBd); polycyclic aromatic hydrocarbons; PCBs; and of PCDD and PCDF homologs and their toxic isomers. This suggests that there are ongoing contaminant inputs within the Cole Drain system. A number of these chlorinated contaminants have been disposed of in landfills bordering the Cole Drain-Scott Road Ditch system (e.g., the Dow Chemical Scott Road landfill). The detection of high concentrations of chlorinated aliphatics and aromatics in the Polysar Flyash Pond Drain and the Scott Road Drain (which contains leachate from the Dow Scott Road Landfill) effluents, coupled with the similarity of the Scott Road Drain effluent and the Cole Drain discharge contaminant profiles (again with HCBd dominating), suggests that these two contributing discharges, particularly the Scott Road Drain, are important sources of these organic compounds. Additionally, the similarity of the Cole Drain sediment and the final effluent contaminant profiles suggests that the resuspension or erosion of contaminated sediments and/or soils within the system may also constitute a source of these contaminants. Loadings of these chlorinated aliphatics and aromatics constituted a notable percentage of the total discharge loading of the lower St. Clair River. This also resulted in localized (i.e., within the discharge plume, at least) concentrations in excess of the St. Clair River RAP Environmental Yardsticks and/or the Provincial Water Quality Guidelines for the Protection of Aquatic Life for HCBd,

PentaCB, HCB, and possibly also of aluminum, cadmium, cobalt, phenolics and total phosphorus.

Recommendation: The source(s) of these inputs/losses to the Cole Drain system should be terminated as soon as possible. Success in the identification and elimination of contaminants sources as part of recent remedial measures by Dow should be verified as soon as possible. Remedial work should include the removal of contaminated sediments and soils from the drain and its contributing water courses in a manner that will minimize the potential for resuspension and loss of particulate-bound contaminants.

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APPENDIX A
WHOLE-WATER SAMPLES

Table A-6. Correlation analysis (Pearson Product-Moment) results for selected parameters in Cole Drain effluent whole-water samples.

APPENDIX B
PARTICULATES SAMPLES

Table B-9. Correlation analysis (Pearson Product-Moment) results for selected parameters in Cole Drain effluent particulates samples (both surveys).

Table B-9. continued.

Table B-10. Comparison of analytical results for replicate particulates samples.

| Parameter | Concentration Units | Sampling Dates | | | |
|-----------------------------------|---------------------|------------------------|-----------------|------------------------|-----------------|
| | | August 23 | | August 24 | |
| | | Mean & Range | % Coeff. Var'n. | Mean & Range | % Coeff. Var'n. |
| Moisture | % | 78 (77 - 79) | 0.9 | 78 (78 - 78) | 0.0 |
| Very Coarse Sand, <2000,>1000 µm | " | 0.0 (0.0 - 0.0) | 0.0 | 0.0 (0.0 - 0.0) | 0.0 |
| Coarse-Very Fine Sand, <99,>62 µm | " | 24 (22 - 26) | 12 | 23.5 (22 - 25) | 9.0 |
| Total Silt, <62,>3.73 µm | " | 66.8 (65.3 - 68.2) | F | 67.1 (65.1 - 69.0) | 4.1 |
| Total Clay, <3.73,>0.17 µm | " | 9.2 (9.0 - 9.4) | 3.1 | 9.8 (9.8 - 9.8) | 0.0 |
| Coarse Sand, <999,>704 µm | " | 0.2<W (0.2<W - 0.2<W) | -- | 0.2<W (0.2<W - 0.2<W) | -- |
| Coarse Sand, <704,>500 µm | " | 0.2<W (0.2<W - 0.2<W) | -- | 0.2<W (0.2<W - 0.2<W) | -- |
| Medium Sand, <500,>352 µm | " | 0.5<W (0.5<W - 0.5<W) | -- | 0.5<W (0.5<W - 0.5<W) | -- |
| Medium Sand, <352,>250 µm | " | 1.0<W (1.0<W - 1.0<W) | -- | 1.0<W (1.0<W - 1.0<W) | -- |
| Fine Sand, <250,>176 µm | " | 1.0<W (1.0<W - 1.0<W) | -- | 1.0<W (1.0<W - 1.0<W) | -- |
| Fine Sand, <176,>125 µm | " | 2.0 (0.5<W - 4.0) | 141 | 2.5 (1.7<T - 3.2) | 43 |
| Very Fine Sand, <125,>88 µm | " | 9.2 (8.0 - 10.4) | 18 | 9.5 (8.3 - 10.7) | 18 |
| Very Fine Sand, <88,>62 µm | " | 12.75 (11.6 - 13.9) | 13 | 11.4 (11.3 - 11.5) | 1.2 |
| Coarse Silt, <62,>42.2 µm | " | 14.0 (13.2 - 14.8) | 8.1 | 13.6 (13.0 - 14.1) | 5.7 |
| Coarse Silt, <42.2,>29.8 µm | " | 12.45 (12.0 - 12.9) | 5.1 | 12.65 (12.2 - 13.1) | 5.0 |
| Medium Silt, <29.8,>21.1 µm | " | 10.95 (10.7 - 11.2) | 3.2 | 11.1 (10.7 - 11.5) | 5.1 |
| Medium Silt, <21.1,>14.9 µm | " | 8.8 (8.7 - 8.9) | 1.6 | 8.8 (8.5 - 9.1) | 4.8 |
| Fine Silt, <14.9,>10.5 µm | " | 7.1 (7.1 - 7.1) | 0.0 | 7.1 (7.0 - 7.2) | 2.0 |
| Fine Silt, <10.5,>7.46 µm | " | 5.45 (5.4 - 5.5) | 1.3 | 5.5 (5.5 - 5.5) | 0.0 |
| Very Fine Silt, <7.46,>5.27 µm | " | 4.35 (4.3 - 4.4) | 1.6 | 4.45 (4.4 - 4.5) | 1.6 |
| Very Fine Silt, <5.27,>3.73 µm | " | 3.55 (3.5 - 3.6) | 2.0 | 3.75 (3.7 - 3.8) | 1.9 |
| Coarse Clay, <3.73,>2.63 µm | " | 2.75 (2.7 - 2.8) | 2.6 | 2.95 (2.9 - 3.0) | 2.4 |
| Coarse Clay, <2.63,>1.69 µm | " | 2.3 (2.2 - 2.4) | 6.1 | 2.5 (2.4 - 2.6) | 5.7 |
| Medium Clay, <1.69,>1.01 µm | " | 1.6 (1.5 - 1.7) | 8.8 | 1.75 (1.7 - 1.8) | 4.0 |
| Fine Clay, <1.01,>0.66 µm | " | 0.85<T (0.8<T - 0.9<T) | 8.3 | 0.9<T (0.9<T - 0.9<T) | 0.0 |
| Fine Clay, <0.66,>0.43 µm | " | 0.6 (0.6 - 0.6) | 0.0 | 0.65 (0.6 - 0.7) | 11 |
| Very Fine Clay, <0.43,>0.34 µm | " | 0.3<T (0.3<T - 0.3<T) | 0.0 | 0.25<T (0.2<T - 0.3<T) | 28 |
| Very Fine Clay, <0.34,>0.21 µm | " | 0.45<T (0.4<T - 0.5) | 16 | 0.45<T (0.4<T - 0.5) | 16 |
| Very Fine Clay, <0.21,>0.17 µm | " | 0.35<T (0.3<T - 0.4<T) | 20 | 0.35<T (0.3<T - 0.4<T) | 20 |
| Calcium | mg.kg ⁻¹ | 47000 (45000 - 49000) | 6.0 | 41000 (40000 - 42000) | 3.4 |
| Chloride | " | 115 (110 - 120) | 6.1 | 105 (100 - 110) | 6.7 |
| Loss on Ignition | g.kg ⁻¹ | 250 (240 - 260) | 5.7 | 250 (240 - 260) | 5.7 |
| Carbon, total Organic | " | 115 (110 - 120) | 6.1 | 115 (110 - 120) | 6.1 |
| Magnesium | mg.kg ⁻¹ | 20500 (20000 - 21000) | 3.4 | 18000 (18000 - 18000) | 0.0 |
| Nitrogen, total Kjeldahl | g.kg ⁻¹ | 15.5 (15 - 16) | 4.6 | 17.0 (16 - 18) | 8.3 |
| Phosphorus, total | g.kg ⁻¹ | 15.0 (15 - 15) | 0.0 | 17.0 (16 - 18) | 8.3 |

| Parameter | Concentration Units | Sampling Dates | | | |
|----------------------------|------------------------|-----------------------|-----------------|-----------------------|-----------------|
| | | August 23 | | August 24 | |
| | | Mean & Range | % Coeff. Var'n. | Mean & Range | % Coeff. Var'n. |
| Potassium | mg.kg ⁻¹ | 2400 (2400 - 2400) | 0.0 | 2600 (2600 - 2600) | 0.0 |
| Sodium | " | 535 (520 - 550) | 4.0 | 540 (540 - 540) | 0.0 |
| Solvent Extractables | mg.kg ⁻¹ | 13313 (13035 - 13591) | 2.9 | 13212 (12648 - 13776) | 6.0 |
| Aluminum | mg.kg ⁻¹ | 48500 (45000 - 52000) | 10 | 51000 (47000 - 55000) | 11 |
| Arsenic | " | 6.8 (6.7 - 6.9) | 1.0 | 7.15 (6.9 - 7.4) | 4.9 |
| Barium | " | 88 (86 - 90) | 3.2 | 88.5 (85 - 92) | 5.6 |
| Beryllium | " | 0.5<W (0.5<W - 0.5<W) | — | 0.5<W (0.5<W - 0.5<W) | -- |
| Cadmium | " | 5.75 (2.7 - 8.8) | 75 | 2.95 (2.4 - 3.5) | 26 |
| Chromium | " | 165 (160 - 170) | 4.3 | 170 (160 - 180) | 4.2 |
| Cobalt | " | 87.5 (82 - 93) | 8.9 | 89 (84 - 94) | 7.9 |
| Copper | " | 155 (140 - 170) | 14 | 160 (160 - 160) | 0.0 |
| Iron | " | 17000 (17000 - 17000) | 0.0 | 18500 (18000 - 19000) | 3.8 |
| Lead | " | 39.5 (35 - 44) | 16 | 36.5 (36 - 37) | 1.9 |
| Manganese | " | 390 (390 - 390) | 0.0 | 395 (390 - 400) | 1.8 |
| Mercury | " | 0.425 (0.40 - 0.45) | 8.3 | 0.445 (0.42 - 0.47) | 7.9 |
| Molybdenum | " | 3.4 (3.4 - 3.4) | 0.0 | 4.15 (4.1 - 4.2) | 1.7 |
| Nickel | " | 150 (140 - 160) | 4.7 | 155 (150 - 160) | 4.6 |
| Strontium | " | 89.5 (88 - 91) | 2.4 | 72 (70 - 74) | 3.9 |
| Titanium | " | 120 (120 - 120) | 0.0 | 110 (110 - 110) | 0.0 |
| Vanadium | " | 23.5 (23 - 24) | 3.0 | 26 (26 - 26) | 0.0 |
| Zinc | " | 315 (300 - 330) | 6.7 | 315 (300 - 330) | 6.7 |
| Hexachloroethane | µg.kg ⁻¹ | 14.5 (14 - 15) | 4.9 | 15.5 (11 - 18) | 44 |
| Hexachlorobutadiene | " | 2000 (1800 - 2200) | 19 | 2150 (1900 - 2400) | 21 |
| 1,2,4-Trichlorobenzene | " | 28 (20 - 36) | 40 | 29 (26 - 32) | 15 |
| 1,3,5-Trichlorobenzene | " | 68 (56 - 80) | 30 | 84 (78 - 90) | 7.1 |
| 1,2,3,5-Tetrachlorobenzene | " | 25 (20 - 30) | 28 | 30 (30 - 30) | 0.0 |
| 1,2,4,5-Tetrachlorobenzene | " | 50 (50 - 50) | 0.0 | 45 (40 - 50) | 16 |
| Pentachlorobenzene | " | 114.5 (99 - 130) | 19 | 113 (96 - 130) | 21 |
| Hexachlorobenzene | " | 745 (390 - 1100) | 67 | 475 (360 - 590) | 34 |
| Octachlorostyrene | " | 600 (600 - 600) | 0.0 | 655 (560 - 750) | 21 |
| Total PCBs | " | 80 (80 - 80) | 0.0 | 130 (120 - 140) | 5.4 |
| Acenaphthene | µg.kg ⁻¹ | 20<W (20<W - 20<W) | -- | 20<W (20<W - 20<W) | -- |
| Acenaphthylene | " | 20<W (20<W - 20<W) | -- | 20<W (20<W - 20<W) | -- |
| Anthracene | " | 70<T (60<T - 80<T) | 10 | 70 (60<T - 80<T) | 10 |
| Benzo(a)Anthracene | " | 110 (100 - 120) | 6.4 | 130 (120 - 140) | 11 |
| Benzo(b)Fluoranthene | " | 110 (100 - 120) | 6.4 | 140 (120 - 160) | 20 |
| Benzo(k)Fluoranthene | " | 40<T (40<T - 40<T) | 0.0 | 40<T (40<T - 40<T) | 0.0 |
| Benzo(g,h,i)Perylene | " | 100<T (80<T - 120<T) | 28 | 100<T (80<T - 120<T) | 28 |

| Parameter | Concentration Units | Sampling Dates | | | |
|-------------------------|------------------------|---------------------|-----------------|-----------------------|-----------------|
| | | August 23 | | August 24 | |
| | | Mean & Range | % Coeff. Var'n. | Mean & Range | % Coeff. Var'n. |
| Benzo(a)Pyrene | " | 100 (80<T - 120<T) | 28 | 120<T (120<T - 120<T) | 0.0 |
| Chrysene | " | 180 (160 - 200) | 16 | 210 (200 - 220) | 6.7 |
| Dibenzo(a,h)Anthracene | " | 80<T (40<W - 120<T) | 141 | 40<W (40<W - 40<W) | -- |
| Fluoranthene | µg.kg ⁻¹ | 220 (180 - 260) | 26 | 260 (240 - 280) | 11 |
| Fluorene | " | 20<W (20<W - 20<W) | -- | 20<W (20<W - 20<W) | -- |
| Indeno(1,2,3-cd)Pyrene | " | 300 (280 - 320) | 9.4 | 280 (240 - 320) | 20 |
| Naphthalene | " | 50<T (40<T - 60<T) | 28 | 50<T (40<T - 60<T) | 28 |
| Phenanthrene | " | 210 (180 - 240) | 20 | 250 (240 - 260) | 5.7 |
| Pyrene | " | 230 (200 - 260) | 18 | 280 (260 - 300) | 10 |
| TetraCDF | ng.kg ⁻¹ | 49.5 (26 - 73) | 67 | 88.5 (86 - 91) | 4.0 |
| TetraCDD | " | 3.8 (1< - 7.6) | 141 | 5.4 (4.4 - 6.4) | 13 |
| PentaCDF | " | 110 (110 - 110) | 0.0 | 120 (110 - 130) | 12 |
| PentaCDD | " | 31.5 (28 - 35) | 16 | 32.5 (23 - 42) | 41 |
| HexaCDF | " | 130 (130 - 130) | 0.0 | 150 (150 - 150) | 0.0 |
| HexaCDD | " | 67 (64 - 70) | 6.3 | 59.5 (48 - 69) | 25 |
| HeptaCDF | " | 115 (110 - 120) | 6.1 | 125 (110 - 140) | 17 |
| HeptaCDD | " | 145 (140 - 150) | 4.9 | 160 (140 - 180) | 18 |
| OctaCDF | " | 485 (450 - 520) | 10 | 535 (520 - 550) | 4.0 |
| OctaCDD | " | 420 (390 - 450) | 9.0 | 485 (430 - 540) | 16 |
| 2,3,7,8-TetraCDF | " | 14.5 (12 - 17) | 22 | 17.5 (16 - 19) | 12 |
| 2,3,7,8-TetraCDD | " | 1.5< (1< - 2<) | -- | 2< (2< - 2<) | -- |
| 1,2,3,7,8-PentaCDF | " | 10.5 (10 - 11) | 6.7 | 10.5 (10 - 11) | 6.7 |
| 2,3,4,7,8-PentaCDF | " | 14.5 (14 - 15) | 4.9 | 15 (15 - 15) | 0.0 |
| 1,2,3,7,8-PentaCDD | " | 5.4 (5.0 - 5.8) | 10 | 5.7 (5.4 - 6.0) | 7.4 |
| 1,2,3,4,7,8-HexaCDF | " | 34 (33 - 35) | 2.1 | 39 (37 - 41) | 7.3 |
| 1,2,3,6,7,8-HexaCDF | " | 17 (16 - 18) | 8.3 | 19 (19 - 19) | 0.0 |
| 2,3,4,6,7,8-HexaCDF | " | 4< (5< - 8.0) | 141 | 3< (4< - 5.8) | 141 |
| 1,2,3,7,8,9-HexaCDF | " | 3< (1< - 4<) | -- | 1< (5< - 2.7) | 141 |
| 1,2,3,4,7,8-HexaCDD | " | 4.1 (3.3 - 4.9) | 28 | 4.9 (4.5 - 5.3) | 12 |
| 1,2,3,6,7,8-HexaCDD | " | 6.3 (5.6 - 7.0) | 16 | 6.35 (6.0 - 6.7) | 7.8 |
| 1,2,3,7,8,9-HexaCDD | " | 5.65 (5.5 - 5.8) | 3.8 | 4.6 (4.2 - 5.0) | 12 |
| 1,2,3,4,6,7,8,-HeptaCDF | " | 47 (46 - 48) | 3.0 | 48.5 (46 - 51) | 7.3 |
| 1,2,3,4,7,8,9-HeptaCDF | " | 8.3 (7.9 - 8.7) | 6.8 | 9.2 (8.8 - 9.6) | 4.3 |
| 1,2,3,4,6,7,8-HeptaCDD | " | 65 (61 - 69) | 8.7 | 73.5 (63 - 84) | 20 |

NOTES: CV = $[\sqrt{2(\max. - \min.)} / (\max. + \min.)] \times 100$.

Samples with no detectable concentrations were assigned "zero" for calculation purposes.

APPENDIX C

IMPORTANT COLE DRAIN CONTAMINANTS - THEIR USES AND POTENTIAL SOURCES

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-----------------|---|--|---|-------------------------------|---|---|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Chloride | -CaCl ₂ & halite [NaCl] | | -Cl ₂ , in manuf. of plastics, chlorinated hydrocarbons (e.g., vinyl chloride) & synthetic rubber (Budavari, 1996) -Cl ₂ O ₇ , catalyst in cellulose esterification (ibid) -ClF ₃ , fluorinating agent & pyrolysis inhibitor for fluorocarbon polymers (ibid) | as chlorine, for disinfection | as chlorine, for disinfection | -NaCl used in manuf. of Cl ₂ , NaHCO ₃ , Na ₂ CO ₃ , NaClO ₃ , NaClO ₂ , NaOH, NaClO.5H ₂ O (CCREM, 1987) -bleaching cellulose, paper-pulp, flour, leather, fats, oils, textiles, beeswax; cleaning & de-tanning leather; oxidizing agent, bactericide, antiseptic & deodorizer; de-tinning & de-zincing iron (Budavari, 1996) -in storm water runoff & some industrial discharges |
| Nitrogen (TKN) | -major atmospheric constituent -as nitrates in mineral deposits -important component of plants & animals | | -NO ₂ , or N ₂ O ₅ , in nitration of organic compounds, e.g., chloroform (Budavari, 1996) -HNO ₃ , oxidizing agent in organic reactions (ibid) -NO, stabilizer for propylene, methyl ether (ibid) | | as NH ₃ , NO ₃ or NO ₂ in effluent | -manuf. ammonia, nitric acid, nitrates, nitrites, cyanides, explosives; used as inert gas & liquid for fast freezing (Budavari, 1996) -NO ₂ , intermediate in nitric & sulfuric acid manuf.; in rocket fuels (ibid) -in storm water runoff & some industrial discharges -as NO ₃ , in waste disposal dumps or landfills leachate (CCREM, 1987) |
| Phosphorus (TP) | -as phosphates in chlorapatite [Ca ₅ (PO ₄) ₃ Cl], fluorapatite [Ca ₅ (PO ₄) ₃ F], vivianite [Fe ₃ (PO ₄) ₃ Cl], wavelite [Al ₃ (PO ₄) ₂ (OH) ₃ ·(H ₂ O) ₅] (Stecher, 1968) -important component of plants & animals | -P ₂ S ₅ , in manuf. of lubricating oil additives (Budavari, 1996) | -POCl ₃ , PCl ₃ & PCl ₅ , chlorinating agents (Budavari, 1996) -P ₂ O ₅ , condensing agent (ibid) -PCl ₅ , catalyst in manuf. of acetyl cellulose (ibid) -PF ₅ & PF ₃ , catalysts in ionic polymerizations (ibid) -P ₂ S ₅ , sulfidization agent (ibid) | | in effluent | in storm water runoff & some industrial discharges (CCREM, 1987) -manuf. of fertilizers, pesticides, phosphoric acid, phosphine, phosphoric anhydride, PCl ₅ , PCl ₃ , smoke bombs, safety matches, used in pyrotechnics, drying and dehydrating agents (Budavari, 1996) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|--|---|--|---|---|---|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Aluminum | -bauxite [Al ₂ O ₃], cryolite [Na ₃ AlF ₆], feldspar [XAl ₍₁₋₂₎ Si ₍₃₋₂₎ O ₈], or aluminosilicates e.g., kaolin [H ₄ Al ₂ Si ₂ O ₉] in all rock types, most geologic materials, particularly clays (CCREM, 1987; OME, 1988) -trace contaminant in fossil fuels (CCREM, 1987) | -AlCl ₃ , catalyst in manuf. of ethyl benzene (OME, 1988; Wittcoff & Reuben, 1996) -anhydrous AlCl ₃ , in cracking petroleum; manuf. of rubbers & lubricants (Budavari, 1996) -hexahydrate AlCl ₃ , in refining crude oil (ibid) -AlB ₃ H ₁₂ , in jet engine & rocket fuels (ibid) -Al(OH) ₃ , in manuf. of lubricants (ibid) -Al palmitate & Al oleate, thickeners for petroleum & lubricants (ibid) -Al oleate, in high-pressure & high-temperature greases (ibid) -Al stearate, thickener for lubricating oils (ibid) -Al ₂ (SO ₄) ₃ , clarifying oils & fats; deodorizing & decolorizing petroleum (ibid) | -AlCl ₃ , Al(OC ₂ H ₅) ₃ , AlH ₃ & Al ₂ O ₃ .B ₂ O ₃ , polymerization catalysts (OME, 1988; Budavari, 1996) -anhydrous AlCl ₃ , in manuf. of rubbers (Budavari, 1996) - Al ₂ CaH ₈ , & AlH ₄ Li, reducing agents for aldehydes, ketones & acid chlorides; in reduction of esters to alcohols, nitriles to amines, aromatic nitro compounds to azo compounds (ibid) -Al(OC ₂ H ₅) ₃ , in reduction of aldehydes & ketones (ibid) -Al alkyls, polymerization catalysts & intermediates in organic syntheses (ibid) -AlB ₃ H ₁₂ & AlH ₃ , reducing agents (ibid) -AlBr ₃ , acid catalyst in organic syntheses (ibid) -Al[OC(CH ₃) ₃] ₃ , reagent for oxidation of alcohols to ketones; in dealcoholation of orthoesters (ibid) -Al ₄ C ₃ , for generation methane (ibid) -AlF ₃ , & AlI ₃ , catalysts in organic reactions (ibid) -Al[OCH(CH ₃) ₂] ₃ , in alcoholysis & ester exchange; synthesis of higher alkoxides, chelates & acylates (ibid) | -KAl(SO ₄) ₂ (potassium alum), used in purifying water to control pH & as flocculating agent for suspended solids (CCREM, 1987; OME, 1988; Budavari, 1996) | -Al ₂ (SO ₄) ₃ (cake alum), to control pH & precipitate suspended solids & phosphorus (OME, 1988; Budavari, 1996) | -emitted from secondary Al smelters & as a by-product of coal combustion (CCREM, 1987) -used in ammonia synthesis, manuf. of Al alloys & steel, inks, paints, lacquer, glass, ceramics, fire clay, adhesives, dental cements, abrasives, explosives, electrical components, parchment paper; artificial gems, in semiconductor research; in foam fire extinguishers, pesticides & embalming fluids (Budavari, 1996) -leather tanning & sizing, glazing paper, electrolytic Cu plating, textile dyeing mordant, textile water & fireproofing, as absorbent & corrosion inhibitor, desiccant, chromatographic matrix, disinfectant, fumigant, antiperspirant, wood preservative, hardening agent, metallurgical flux, as suspending and thickening agents, nitrating agent, used in uranium extraction (ibid) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|--|---|--|-----|--|---|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Cadmium | -greenockite [CdS], in non-ferrous copper, lead & zinc ores, & in some phosphate rocks used for fertilizers (CCREM, 1987) -trace contaminant in fossil fuels (Förstner & Wittman, 1983) | -CdCl ₂ & CdI ₂ as lubricants (CCREM, 1987; Budavari, 1996) | -Cd stearate, stabilizer in polyvinyl chloride & synthetic rubber mfg. (Förstner & Wittman, 1983; CCREM, 1987) -CdO & CdWO ₄ , catalysts for organic reactions (Budavari, 1996) -CdS, for colouring rubber (ibid) | | corrosion of pipes in water supply system (Förstner & Wittman, 1983) | -by-product of primary Cu, Ni & Zn production & manuf. of iron & steel (CCREM, 1987) -used in Cd electroplating, Cd, Cu & Ni electro deposition, Cu hardening, Ni-Cd batteries, photoelectric cells, electronics, optics, pigments, dyeing, photography, engraving, lithography, alloys, soft solder, reactor control rods, fungicide, nematocide, ceramic paints, manuf. of phosphors, semiconductor research, fireworks, scintillation counters (Budavari, 1996) -agricultural use of Cd-containing sludges, fertilizers & pesticides (CCREM, 1987) -emitted as a by-product of fuel combustion in stationary sources (ibid) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|--|--|---|-----|-----|--|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Chromium | <ul style="list-style-type: none"> -in chromite [FeCr₂O₄] deposits (Stecher, 1968) -trace contaminant in fossil fuels (Förstner & Wittman, 1983) | <ul style="list-style-type: none"> -CrO₃, catalyst in purifying oil & acetylene (Budavari, 1996) -CrF₂, in catalytic cracking of hydrocarbons (ibid) -CrSO₄, dehydrohalogenating & reducing agent (ibid) -Cr(OH)₃, catalyst in dehydrogenation of alcohols & paraffins, hydrogenation of olefins (ibid) -CrPO₄, catalyst in dehydrogenation of hydrocarbons or polymerization of olefins (ibid) -Cr(CO)₆, gasoline additive (ibid) | <ul style="list-style-type: none"> -Cr acetate, CrCl₃ & CrBr₃, catalysts in olefin polymerization (Budavari, 1996) -Cr(CO)₆, catalysts in olefin polymerization & isomerization (ibid) -CrO₂F₂, fluorination catalyst (ibid) -CrO₂Cl₂, catalyst for olefin polymerization, oxidation of hydrocarbons, for aldehyde and ketone prod'n. (ibid) -Cr acetate, oxidation catalyst (ibid) -CrF₃, halogenation catalyst (ibid) -CrF₂, alkylation catalyst (ibid) -Cr₂(SO₄)₃, to improve dispersability of vinyl polymers in water (ibid) -CrO₃, oxidizing agent (ibid) -CrCl₂, in catalysts for organic reactions (ibid) -Cr formate, in catalysts for organic reactions (ibid) | | | <ul style="list-style-type: none"> -used in leather tanning, as wood preservative (USDHHS, 1993; Budavari, 1996) -in manuf. of Fe-Cr or Fe-Ni-Cr alloys, in cement, refractory materials manuf., in dyes & pigments for paints, glazes, Cr plating, Cu stripping, Al anodizing (Budavari, 1996) -in photographic emulsions, as textile dyeing mordant, corrosion inhibitors, abrasives, mothproofing & waterproofing agents, colouring & hardening marble, polishing metals (ibid) -use of Cr-containing fertilizers & pesticides (Förstner & Wittman, 1983; CCREM, 1987) -emitted as a by-product of coal & oil combustion (CCREM, 1987) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|---|--|---|-----|-----|--|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Cobalt | -as cobaltite [CoAsS] & skutterudite [(CoNiFe)As] ores -trace contaminant in fossil fuels (Förstner & Wittman, 1983) | component of hydro treating catalyst (Wittcoff & Reuben, 1996) -CoS, catalyst for hydrogenation & hydrodesulfurization (Budavari, 1996) | -Co(C ₂ H ₃ O ₂) ₃ , cobaltic acetate, catalyst in cumene hydro peroxide decomposition (Budavari, 1996) -Co(C ₂ H ₃ O ₂) ₂ , cobaltous acetate, catalyst for oxidation & esterification (ibid) -CoF ₃ , hydrocarbon fluorinating agent (ibid) -K ₃ Co(NO ₂) ₆ ·1.5H ₂ O, in colouring rubber (ibid) -CoBr ₂ , CoF ₂ & CoI ₂ , catalysts for organic reactions (ibid) -Co ₃ (PO ₄) ₂ , used in plastic resins (ibid) | | | -binder in tungsten carbides i.e., abrasives, foam stabilizer for beer & malt beverages, fertilizer & feed additive, in manuf. of catalysts & Vitamin B ₁₂ (Budavari, 1996) -in paint, enamel, glass, glaze, ceramics pigments, ink, cement additive, oxidation catalysts, used in electroplating (ibid) -in hygrometers & semi-conductors, storage batteries, Co-electroplating (ibid) -in mfg. of alloys & tires, anodizing (CCREM, 1987; Fletcher <i>et al.</i> , 1995a; Budavari, 1996) -emitted as a by-product of coal & oil combustion (CCREM, 1987) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|--|---|--|-----|---|--|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Copper | -chalcocite [Cu ₂ S], bornite [Cu ₅ FeS ₄], chalcopyrite [CuFeS ₂] ores -trace contaminant in fossil fuels (Förstner & Wittman, 1983) | -CuCr ₂ O ₄ , selective hydrogenation catalyst (Budavari, 1996) -Cu(CH ₃ CH ₂ -CH ₂ COO) ₂ , cupric butyrate, used in some lubricants & catalysts (ibid) -CuCO ₃ .Cu(OH) ₂ , cupric carbonate (basic), for sweetening of petroleum sour crude stock (ibid) -CuCl ₂ or CuCl, decolourizing, deodorizing, desulfurizing & purifying agent (ibid) -Cu(C ₁₇ H ₃₃ COO) ₂ , cupric oleate, antioxidant in lubricating oils; fuel oil combustion-improver (ibid) -Cu(ClO ₄) ₂ , catalyst for combustion (ibid) -CuSO ₄ used in petroleum refining (ibid) | - catalyst in vinyl chloride manuf. (Wren <i>et al.</i> , 1990a) -Cu(CH ₃ COO) ₂ , cupric acetate & Cu(C ₁₇ H ₃₃ COO) ₂ , cupric stearate, catalysts in rubber aging (Budavari, 1996) -CuBr ₂ , brominating agent (ibid) -CuCl ₂ , oxidizing agent for aniline dyestuffs & manuf. of acrylonitrile (ibid) -CuF ₂ , fluorinating agent (ibid) -CuS, for devel. of aniline black dye (ibid) -Cu(NO ₃) ₂ , nitrating agent for aromatic organosilicon compds. (ibid) -Cu(C ₁₇ H ₃₃ COO) ₂ , cupric oleate, stabilizer for amide polymers (ibid) -CuC ₂ O ₄ , cupric oxalate, stabilizer for acetylated polyformaldehyde (ibid) -Cu <i>p</i> -phenol sulfonate, esterification catalyst (ibid) -Cu[C ₆ H ₄ (OH)COO] ₂ , cupric salicylate, in separation of mono- from di- or poly- olefinic hydrocarbons (ibid) -CuSO ₄ used in prep'n of azo dyes (ibid) -CuWO ₄ , CuCN & CuSO ₃ , polymerization catalysts (ibid) -CuO, Cu ₃ (PO ₄) ₂ , CuBr, CuCl, CuI, catalysts for organic reactions (ibid) | | -in some fertilizers & pesticides (runoff) -from corrosion of water supply pipes -in sewage sludge (Förstner & Wittman, 1983) | -bactericide, algicide, fungicide, insecticide, molluscicide, rodenticide, wood preservative, fertilizer, used in rectifiers & photoelectric cells, ceramics, paint, varnish, glass & ink pigments, solid-electrolyte, batteries & electrodes, brazing pastes, welding fluxes, feed additive, Cu-electroplating (Budavari, 1996) -in alloys, as heat and electrical conductor (Yule, 1978) -mordant in textile dyeing & printing, in photography, electroplating, pyrotechnics, manuf. of rayon, colouring copper, iron & zinc products, as emulsifier & dispersant, dyeing & hardening marble, tanning leather (Budavari, 1996) -by-product of coal combustion (Förstner & Wittman, 1983) -emitted as a by-product of coal & oil combustion () |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|--|--|--|---|---|---|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Iron | -hematite [Fe ₂ O ₃], magnetite [Fe ₃ O ₄], marcasite [FeS ₂], pyrrhotite (FeS), pyrite [FeS ₂] ores | -FeS, in lubricant coatings (Budavari, 1996) -Fe(CO) ₅ , antiknock agent in motor fuels (ibid) | - used in plastics mfg. (CCREM, 1987) -FeBr ₃ , catalyst for bromination of aromatic compounds (Budavari, 1996) -FeCl ₃ , oxidizing agent in dye manuf. (ibid) -Fe ₄ [Fe(CN) ₆] ₃ , rubber & plastic pigment (ibid) -Fe ₂ O ₃ , pigment for rubber (ibid) -Fe ₂ (SO ₄) ₃ , FeBr ₂ & FeSO ₄ , polymerization catalysts (ibid) -C ₁₀ H ₁₀ Fe, gasoline antiknock additive (ibid) -FeBr ₃ , FeCl ₃ , FeF ₂ & FeI ₂ , catalysts in organic reactions (ibid) -FeC ₂ O ₄ , plastic pigment (ibid) -Fe(CO) ₅ , catalyst & reagent in organic reactions (ibid) | -FeSO ₄ , used in water treatment (Budavari, 1996) -Fe(OH) ₃ , used in purifying water (ibid) -Fe ₂ (SO ₄) ₃ , coagulant in water purification (ibid) | -FeCl ₃ , deodorizing sewage & purifying factory effluents (Budavari, 1996) -Fe ₂ (SO ₄) ₃ , coagulant in sewage treatment (ibid) | -mordant in textile dyeing & printing, wood preservative, fireproofing of synthetic fibres, herbicide, pesticide, leather dye, weighting silk & felt, used in photoengraving & photography, pigments for inks, ceramics, glass, paints, linoleum, leather cloth, carbon papers & carbon ribbons, fertilizer, food & feed supplement, electroplating, Al etching, in Cu & stainless steel pickling, engraving, lithography, chlorinating Ag & Cu ores, preservation of silage (Budavari, 1996) -leather tanning (Yule, 1978) -in magnets, polishing agents & electrical resistors, cathodes & semiconductors (ibid; CCREM, 1987) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|--|---|---|-----|-----|---|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Lead | -galena [PbS], cerussite [PbCO ₃] & anglesite [PbSO ₄] ores (Stecher, 1968) -trace contaminant in fossil fuels (Förstner & Wittman, 1983) | -Pb-(C ₁₈ H ₃₃ O ₂) ₂ , lead oleate, or Pb-(C ₁₈ H ₃₅ O ₂) ₂ , lead stearate, in extreme pressure lubricants (Budavari, 1996) | -Pb ₃ (PO ₄) ₂ , stabilizer for styrene & casein plastics (Budavari, 1996) -PbO ₂ , oxidizing agent in manuf of dyes & rubber substitutes (Stecher, 1968) -PbF ₄ , proposed hydrocarbon fluorinating agent (Budavari, 1996) -PbO, rubber pigment (ibid) -Pb(C ₂ H ₃ O ₂) ₂ .2Pb(OH) ₂ , lead subacetate, for clarifying & decolorizing solutions of organic substances (ibid) -Pb(CH ₃ COO) ₄ , lead tetraacetate, selective oxidizing agent in organic syntheses (ibid) | | | -tank linings; in paint pigments, varnishes, antifouling paints, glazes & plasters, gasoline additive, in alloys incl. solder, storage & galvanic batteries, battery electrodes, in ceramics & electronics devices, explosives primer, in insecticides, used in manuf. of colourless glass, matches, putty & lead carbonate paper (Stecher, 1968) -mordant in dyeing & printing of textiles, weighting silks, used in pyrotechny, photography -radiation shields, electrical cable coverings, ammunition (Yule, 1978) -emitted as a by-product of coal combustion & cement production (Förstner & Wittman, 1983) |
| Manganese | -minerals pyrolusite [MnO ₂], braunite [(Mn ⁺²)(Mn ⁺³) ₆ SiO ₁₂] hausmannite [(Mn ⁺²)(Mn ⁺³) ₂ O ₄], manganite [MnO(OH)] (Stecher, 1968) | -Mn ₂ (CO) ₁₀ , fuel antiknock additive (Budavari, 1996) -methylcyclopentadienyl manganese tricarbonyl (MMT), fuel antiknock agent (WHO, 1981) | - catalyst in chlorination of organic compounds (USDHHS, 1991; WHO, 1981) -MnF ₃ , fluorinating agent (Budavari, 1996) | | | -in several steel & non-ferrous alloys (Budavari, 1996) -in paints, varnishes, glazes, linseed oil, specialty glass, alkaline batteries, feeds & fertilizers, wood preservatives (Budavari, 1996; WHO, 1981) -mordant in textile dyeing & printing, leather tanning, glass de colouring, disinfectant (ibid) -manuf. of amethyst glass (ibid) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|--|--|---|-----|-----|---|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Mercury | -cinnabar [HgS] ore -trace contaminant in fossil fuels (Förstner & Wittman, 1983) | | -Hg(CH ₃ COO) ₂ , mercuric acetate, in absorption of ethylene & mercuration of organic compounds (Budavari, 1996) -HgF ₂ , hydrocarbon fluorinating agent (ibid) -HgS (black), rubber pigment & HgS (red), plastics pigment (ibid) -HgCl ₂ , polymerization catalyst (Yule, 1978) -HgO (red & yellow), reagent & catalyst in organic reactions (ibid) | | | -Hg ₂ Cl ₂ , used in electrodes to produce Cl, NaOH & H ₂ from brine in diaphragm cells (CCREM, 1987; Förstner & Wittman, 1983; Budavari, 1996) -was used in manuf. of barometers, thermometers, hydrometers, pyrometers, Hg arc lamps, calomel electrodes, rectifiers, batteries, paint pigments, antifouling paints, Au & Ag extraction from pyrites, photography intensifier, dental amalgams, fungicide, in preserving specimens, germicide, in some therapeutic medicines & felt hats, brass blackening (Budavari, 1996; CCREM, 1987) -emitted as a by-product of oil combustion (Förstner & Wittman, 1983) |
| Molybdenum | -molybdenite [MoS ₂], powellite [CaO.Mo ₃] & wulfenite [PbMoO ₄] mineral deposits, in bismuth, iron and copper-containing minerals & in coal or uranium deposits Stephenson <i>et al.</i> , 1991b) | -MoS ₂ , used as lubricating oil additive (Förstner & Wittman, 1983; Stephenson <i>et al.</i> , 1991b) & dry lubricant (Budavari, 1996) -component of hydro treating catalyst (Wittcoff & Reuben, 1996) -MoS ₂ , hydrogenation catalyst (Budavari, 1996) | | | | -in printing inks, glazes, lacquers, paints, rubbers, leathers & fertilizers (Stecher, 1968; Stephenson <i>et al.</i> , 1991b; Fletcher <i>et al.</i> , 1995c) -used in manuf. of steel alloys, nonferrous alloys, tungsten, electronic apparatus, glass, ceramics, pigments, fertilizers, smokeless powder & dynamite (CCREM, 1987; Budavari, 1996) -emitted as a by-product of fossil fuel combustion (Stephenson <i>et al.</i> , 1991b) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|--|---|---|-----|-----|---|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Nickel | <p>-pentlandite [(Fe,Ni)₉S₈] ore (Stecher, 1968)</p> <p>-trace contaminant in fossil fuels (Förstner & Wittman, 1983)</p> | <p>-catalyst in oil refining (CCREM, 1987) i.e., component of hydro treating catalyst (Wittcoff & Reuben, 1996)</p> <p>-Ni(CH₃COCHCOCH₃)₂, nickel acetylacetonate, catalyst (Budavari, 1996)</p> | <p>-NiCO₃·2Ni(OH)₂, nickel carbonate hydroxide, catalyst for hardening of fats (Budavari, 1996)</p> <p>-NiCO₄, used in organic synthesis (ibid)</p> | | | <p>-in steel alloys for machinery, industrial plumbing, heat exchangers & petrochemical equipment, Ni-Cd batteries, electrical components, ceramic colours & glazes, in paints, lacquers, cellulose compounds & cosmetics (Budavari, 1996; USDHHS, 1992)</p> <p>-Ni-plating, fabric dyeing & printing mordant; blackening Zn and brass (Budavari, 1996)</p> <p>-emitted as a by-product of coal & oil combustion (Förstner & Wittman, 1983)</p> |
| Vanadium | <p>-vanadinite [Pb₅(VO₄)₃Cl], patronite [VS₄], carnotite [K₂(UO₂)₂(VO₄)₂·3H₂O] ores (Stecher, 1968)</p> <p>-trace contaminant in fossil fuels (Förstner & Wittman, 1983)</p> | <p>-catalyst in petroleum cracking (CCREM, 1987; Stephenson <i>et al.</i>, 1991c)</p> | <p>-catalyst in polymeric plastics manuf. (CCREM, 1987; Stephenson <i>et al.</i>, 1991c)</p> <p>-V₂O₅, catalyst in oxidation of alcohol to acetaldehyde (Budavari, 1996)</p> <p>-V₂O₃, catalyst in manuf. of ethanol from ethylene (ibid)</p> | | | <p>-used in manuf. of steel alloys, aniline black, yellow glass, in dyes, glazes, inks, paints, depolarizer, photographic developer, fabric printing & dyeing mordant (Budavari, 1996; CCREM, 1987)</p> <p>-emitted as a by-product of coal & oil combustion (Förstner & Wittman, 1983)</p> |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|-------------|---|--|--|-----|--|--|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Zinc | -sphalerite (ZnS), zincite [ZnO], willemite [Zn ₂ SiO ₄], franklinite [(Zn,Mn,-Fe)O.Fe.MN ₂ O ₃], gahnite [ZnAl ₂ O ₄] ores (Stecher, 1968) -trace contaminant in fossil fuels (Förstner & Wittman, 1983) | -ZnCl ₂ , used in petroleum refining (Budavari, 1996) | -stabilizer in polyvinyl chloride & synthetic rubber mfg. (Förstner & Wittman, 1983; Wren <i>et al.</i> , 1990b) -ZnF ₂ , in fluorination of organic compounds (Budavari, 1996) -ZnCO ₃ , used in manuf. of rubber (ibid) -ZnCl ₂ , used in vulcanizing rubber (ibid) ZnO, used in manuf. of tires (ibid) -ZnO ₂ , accelerator in rubber compounding & curing agent for synthetic elastomers (ibid) -Zn(C ₁₈ H ₃₅ O ₂) ₂ , zinc stearate, dusting agent for rubber & plastic mold release agent (ibid) -ZnS, rubber pigment (ibid) | | due to corrosion of water supply system pipes (Förstner & Wittman, 1983) | -in dry cell batteries & in protective (galvanizing) coatings for iron & steel, Zn alloys, etching metals & browning steel, electroplating, manuf. parchment paper, in electrical apparatus, wood preservative, in soldering flux, fabric printing & dyeing mordant, glazes, inks, paint, varnish, linoleum & rubber pigments, insecticide, fungicide, in dental cements, deodorant, disinfectant, manuf. crepe & mercerizing cotton, sizing, weighting & crimping fabrics, specimen preservative, fireproofing wood, concrete hardener, for mothproofing, waterproofing agents, bleaching paper (Budavari, 1996) -used in gold extraction, concrete hardening, paper bleaching, electroplating, purifying fats for soaps, photography, manuf. opaque glass & phosphors, matches, white glue (ibid) -emitted as a by-product of coal combustion & zinc production (Förstner & Wittman, 1983) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|------------------------|------------------------------|--|---|---|---|--|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Hexachloroethane | | | -chemical process intermediate during formation of lower mol. weight chlorination products (Howard, 1989) -plasticizer for cellulose esters; minor use in rubber & insecticidal formulations (Verschueren, 1983) | -formed in very small amounts during chlorination of sewage effluent (Howard, 1989) | -formed in very small amounts during chlorination of raw water (Howard, 1989) | -formed during combustion & incineration of chlorinated wastes e.g., PVC (Howard, 1989) -feed additive (Fletcher <i>et al.</i> , 1995b) -used in metal & alloy prod'n., in manuf. of fire extinguishing fluids, smoke candles, pyrotechnics & grenades; moth repellent, fermentation process retardant; camphor substitute in nitro cellulose solvent (Verschueren 1983; Fletcher <i>et al.</i> , 1995b) |
| 1,2,4-Trichlorobenzene | | | -chemical process intermediate & impurity in dichlorobenzenes (McCarty <i>et al.</i> , 1984) -solvent in chemical manuf. - dye & herbicide intermediate (Verschueren, 1983) | | | -dielectric fluid, in synthetic transformer oils, lubricants & insecticides (Verschueren, 1983) |
| Hexachlorobutadiene | | | -waste by-product during manuf. of several chlorinated hydrocarbon solvents (Howard, 1989; McCarty <i>et al.</i> , 1984) - used as solvent for elastomers, natural rubber, synthetic rubber & other polymers; used as chemical intermediate for hydraulic fluids, rubber compounds & fluorinated lubricants (Verschueren, 1983; CCREM, 1987; Yang, 1988) -manuf. in U.S. (Howard, 1989) | | | -used as heat transfer fluid, transformer fluid, hydraulic fluid, gyroscope fluid, wash liquor for removing C ₄ & higher hydrocarbons, & in recovery of Cl from waste gases (Verschueren, 1983; CCREM, 1987; Yang, 1988) -released during refuse combustion & found in fly ash & in road runoff & from disposal sites (Fletcher <i>et al.</i> , 1990; Verschueren, 1983) |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|--------------------|------------------------------|--|--|-----|-----|--|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Pentachlorobenzene | | | <p>-waste by-product formed during manuf. of several chlorinated hydrocarbon solvents (Howard, 1989; McCarty <i>et al.</i>, 1984)</p> <p>-used as intermediate in manuf. of specialty chemicals (McCarty <i>et al.</i>, 1984; Ware & West, 1977, in CCREM, 1987)</p> | | | <p>-impurity in the pesticide pentachloronitrobenzene (Verschueren, 1983)</p> |
| Hexachlorobenzene | | | <p>-plasticizer for polyvinyl chloride (deBarros, 1984)</p> <p>--manuf. in U.S. (Howard, 1989)</p> <p>-used in manuf. of pentachlorophenol, fungicides and fluorocarbons (deBarros, 1984);</p> <p>-by-product formed during manuf. of: vinyl chloride monomer; chlorinated solvents (mainly carbon tetrachloride, perchloroethylene, trichloroethylene, dichloroethylene & dimethyl tetrachloroterephthalate); & pesticides (dacthal, atrazine, simazine, propazine, mirex, pentachlorophenol & pentachloronitrobenzene) (Verschueren, 1983; Howard, 1989; McCarty <i>et al.</i>, 1984)</p> <p>-by-product of electrolytic chlorine or sodium chlorate prod'n. using pitch (Kaminsky & Hites, 1984) or graphite (Verschueren, 1983) anodes</p> <p>-peptizing agent in prod'n of nitroso- & styrene rubbers for tires (Verschueren, 1983)</p> | | | <p>-contaminant in chlorine (Budavari, 1996) & several pesticides, e.g., dichloromethyl tetrachloroterephthalate & pentachloronitrobenzene (Verschueren, 1983)</p> <p>-formerly used as flame retardant & seed fungicide (deBarros, 1984; Budavari, 1996)</p> <p>-fluxing agent in Al smelting, wood preservative, as porosity control in manuf. of graphite anodes (Verschueren, 1983)</p> <p>-used in manuf of pyrotechnics & tracer bullets (Verschueren, 1983)</p> <p>-emitted by waste incineration & found in fly ash (Howard, 1989)</p> |

| Contaminant | Natural Sources or Compounds | Industrial/Municipal Uses and/or Sources | | | | |
|---|---|---|--|-----|-------------------------------|---|
| | | Petroleum | Organic Chemical | WTP | STP | Other |
| Octachlorostyrene | | | by-product of electrolytic chlorine production using pitch electrodes (Kaminsky & Hites, 1984) | | | |
| Polychlorinated Biphenyls (PCBs) | | | -formerly used as plasticizers (deBarros, 1984; CCREM, 1987) | | | -past use as heat transfer fluids, hydraulic fluids solvent extenders, plasticizers, dielectric fluids in capacitors & transformers (deBarros, 1984; CCREM, 1987) -past used in or as lubricants, flame retardants, waterproofing agents, paints, surface coatings, adhesives, printing inks & pesticide extenders (deBarros, 1984; CCREM, 1987) |
| Polycyclic Aromatic Hydrocarbons (PAHs) | -component of some fossil fuels (coal, crude oil) - by-product of wood combustion (e.g., forest fires) | -by-product of petroleum and oil shale refining (e.g., component of refinery still bottoms) | by-product of carbon black mfg. | | present in used crankcase oil | -by-product of uncontrolled & incomplete combustion of organic matter (e.g., fossil fuels, refuse) -by-product of gasification & liquefaction of coal, production of coke, coal tar pitch, asphalt, bitumen and creosote (deBarros, 1984; Verschueren, 1983) -in storm water runoff from paved roads |
| PCDDs & PCDFs | by-products of fossil fuel combustion | | -by-products of vinyl chloride & polyvinyl chloride mfg. (Cleverly, 1997); -PCDFs present in some commercial PCB mixtures (CCREM, 1987) | | | by-products of incineration of municipal, hospital, industrial & hazardous wastes; by-products of chlorophenols & chlorophenoxy herbicides manuf. (Czucwa & Hites, 1984; CCREM, 1987; Rappe 1994) |

NOTES: See Section 7.0 for references cited.

APPENDIX D

CONTAMINANT CONCENTRATIONS IN 1980 AND 1981 COLE DRAIN SYSTEM SAMPLES

