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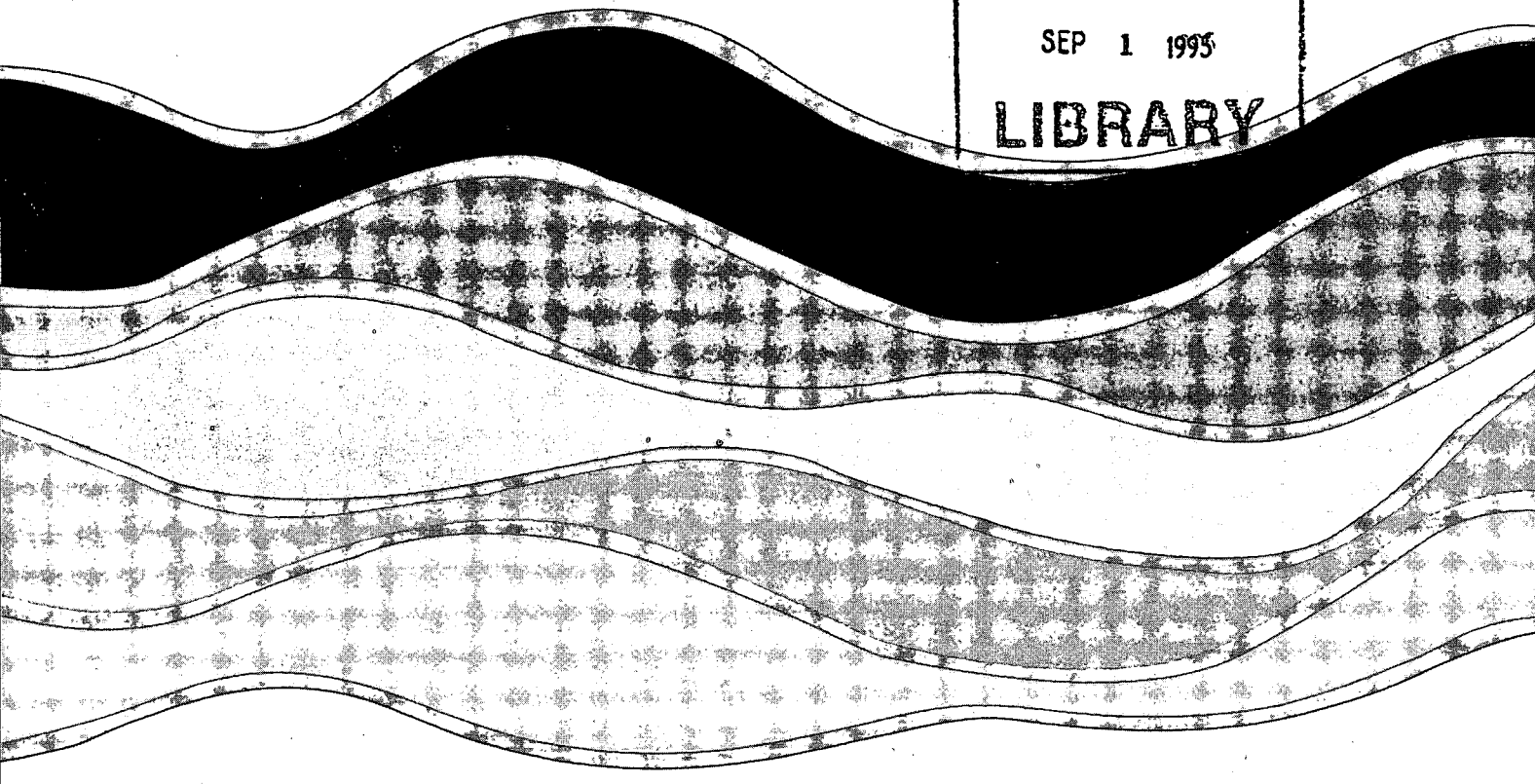

TRACING SEWAGE-CONTAMINATED SEDIMENTS IN HAMILTON HARBOUR USING SELECTED GEOCHEMICAL INDICATORS

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NWRI Contribution No. 94-18

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by

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ABSTRACT

Natural tracers in bottom sediments around the outfall of the Burlington Skyway Sewage Treatment Plant (STP) were analyzed to investigate the pathways of fine contaminated sediments associated with the outfall. The properties examined were: coprostanol and isotope ratios of nitrogen and carbon. The spatial distribution pattern for all the tracers was characterized by extreme values in the vicinity of the outfall, with a systematic decrease with distance. The STP outfall is clearly source for coprostanol as well as for light ^{15}N and heavy ^{13}C. The distribution pattern for coprostanol and $\delta\ ^{15}N$ showed the most consistent transport patterns, while $\delta\ ^{13}C$ patterns were different and might be contaminated by terrestrial carbon from sources other than the STP. Interpretation of the net transport patterns from coprostanol and $\delta\ ^{15}N$ indicates a primary transport trend southward, with a secondary trend northward, curving westward. The net transport patterns inferred from the tracer indicators are compatible with models of 2-dimensional circulation of a buoyant effluent plume, under the effect of the prevailing wind-driven current regime.

INTRODUCTION

Hamilton Harbour is a 21.5 km^2 body of water separated from the western end of Lake Ontario by a narrow sandbar approximately 0.5 km wide (Figure 1). Access to Lake Ontario is via the Burlington Ship Canal (88 m wide by 10 m deep). The Harbour is surrounded by the municipalities of Hamilton, Burlington, and Stoney Creek, and its 500 km^2 watershed is home to approximately 500 000 people. In addition, Hamilton is Canada's major steel and manufacturing centre, and an important shipping port on the St. Lawrence Seaway.

The Harbour is thus a multiple use facility, and receives a variety of municipal and industrial effluents. The concentration of these effluents in such a restricted body of water has had serious consequences insofar as the quality of the water and the bottom sediments in the Harbour are concerned. In fact, Hamilton Harbour has been identified by the International Joint Commission as one of the 42 Areas of Concern in the Great Lakes. Discharges into the Harbour since the 1800's have resulted in widespread deposits of contaminated sediments, especially in the southern sector.

The major sources of suspended sediments and adsorbed contaminants to the Harbour are the 4 sewage treatment plants (STP) serving the surrounding municipalities, the numerous combined sewage overflows (CSO) carrying urban runoff, the two integrated steel mills, and inflowing streams (Figure 1). Of the total discharge into the Harbour, estimated at approximately 3 x 10^6 m^3 day^{-1}, these sources contribute approximately 12%, or 0.4 x 10^6 m^3. Amounts of various contaminants contributed by the STP's and other sources are shown in Table 1.

The effluent from the Burlington Skyway STP (Figure 1), whose outfall is located in 7 m of water in the northeastern corner of the Harbour differs from the others in that it is discharged directly into the Harbour. The others discharge into streams and waterways emptying into the Harbour. The Burlington STP outfall is the one nearest to Burlington Ship Canal, where the main water exchange between Hamilton Harbour and Lake Ontario occurs. Lake Ontario is the source of drinking water for Hamilton and Burlington residents. Standard treatment in the STP reduces the suspended solids load to an annual average of 183 tonnes $year^{-1}$. The aqueous phase, containing much of the dissolved contaminants and nutrients, amounts to 0.07 x 10^6 m^3 day^{-1}. The effluent is discharged at an average annual temperature of 16.3° C, consistently higher than the ambient Harbour water temperature.

Objective

Effluent from the Burlington STP provides a means of identifying long-term patterns of transport for fine sediments circulating through this sector of the Harbour. Because of the large and reactive surface areas of such sediments, they are extremely effective as adsorption and transport platforms for the contaminants found in the sewage effluent. These sediments are transported by hydrodynamic processes over considerable areas in the Harbour, so their transport pathways can assist in interpretation of circulation patterns and areas impacted by

contaminated sediments.

The objective of this study is to identify net transport patterns in Hamilton Harbour for fine contaminated sediments associated with the outfall of the Burlington STP. The adsorbed, sewage-associated geochemical indicators used here as tracers are coprostanol and isotope ratios of nitrogen and carbon. Organic content of the sediments is also investigated as a means of normalizing, and thus enhancing, the coprostanol patterns.

Description of tracer approach and previous work

Tracer techniques, especially radioactive tracers, have been widely used to study fine sediment transport (Coakley and Long 1990). Radioactive tracers are selected either to decay to background (safe) levels or to be diluted to non-hazardous levels, within a limited time. Such tracers are effective for resolving short-term responses of sediment, but they are complicated to manage and are not well suited for long-term and time-integrated transport studies.

Natural, or incidentally-introduced, tracers have considerable advantages over artificial tracers. Natural tracer methods are less expensive, the field work is relatively simple, sampling can be repeated as often as is necessary, and they can be used for intermediate to long term investigations (Salomons and Mook 1987, Coakley and Long 1990, Coakley and Poulton 1991). However, the approach is qualitative, largely because the input rate is unknown and tracer losses and perturbations in the sediments are poorly understood. The key constraint of natural tracers is that they are related directly to a particular source, are conservative (i.e., changes in their concentration are related only to dilution over the transport distance), and are readily quantified in sediments (Coakley and Long, 1990).

Chemical components of sewage have been used in several studies as indicators of sewage contamination. The faecal sterol, coprostanol (5β-cholestan-3β-ol) has proved very valuable as a chemical marker of sewage contamination (Dutka et al. 1974, Hatcher et al. 1977, Hatcher and McGillivary 1979, Brown and Wade 1984, Düreth et al. 1986, Holm and Windsor 1990, Coakley and Poulton 1991, Coakley et al. 1992). Coprostanol is the major faecal sterol of humans, comprising 40 to 60% of the total neutral sterols excreted. Virtually the only source of this chemical is the faeces of man and higher animals. Studies by Hatcher and McGillivary (1979) have demonstrated that coprostanol concentrations in cores were unchanged over 25 years, which shows that it is relatively conservative in anoxic sediments. Hatcher et al. (1977) reported on the distribution of coprostanol in sediments around sewage sludge dump sites in the New York Bight and concluded that coprostanol can be used as a chemical marker for sewage contamination. Similar studies by Brown and Wade (1984), conducted around the outfall of the Chesapeake-Elizabeth STP, confirmed the usefulness of coprostanol in providing a better understanding of the fate of sewage-derived contaminants in areas around sewage outfalls. In investigations of contaminant dispersal associated with an STP outfall near Cocoa, Florida, Holm and Windsor (1990) concluded that mapping the distribution of coprostanol can be a valuable tool for assessing the extent of sewage effluent plume transport, particularly in areas undergoing rapid population growth.

Sediment tracing studies in fresh waters using coprostanol are less common. Düreth

et al. (1986) investigated the relationships existing between coprostanol, faecal indicator bacteria and various physico-chemical, and bacterial stress factors in an ice-covered Finnish lake. Coakley and Poulton (1991) used natural (sewage-related compounds: coprostanol and α-tocopheryl acetate), organic contaminant species (linear n-alkanes), and artificial (cesium) tracers to investigate fine sediment transport in the Toronto area.

Nitrogen isotope ratios ($^{15}N/^{14}N$) have been used to trace the plume of domestic and industrial sewage (Sweeney et al. 1980, Sweeney and Kaplan 1980a, Coakley et al. 1992). The use of nitrogen and carbon isotope ratios as tracers is based on the consistent difference between ratios from terrestrial (sewage outfall) versus aquatic sources. Although the nitrogen isotope ratio is not conservative over the long term (nitrogen undergoes isotopic fractionation when it is consumed as a nutrient), the ratio has been shown to be sufficiently stable for use as a sediment tracer.

Sweeney and Kaplan (1980b) measured nitrogen isotope ratios in marine bottom sediments around domestic and industrial sewage discharged at a depth of 60 m to determine the level of sewage contribution to flocculent suspended material persisting at water depths of 7, 13, and 20 m. They found that the amount of sewage nitrogen present is a function of both depth and distance from the outfall. They concluded that organic nitrogen at 20 m and 13 m depth was predominantly of sewage origin, while that at 7 m was predominantly of marine origin. The nitrogen isotope ratio of organic matter in particulate sewage effluent ($+2.5^0/_{00}$) was found to be significantly lower than that from organic matter in uncontaminated sediment of the same area ($+10^0/_{00}$).

Coakley et al. (1992) used carbon and nitrogen stable isotope ratios in sediments as tracers of STP-contaminated fine sediment dispersal in Lake Ontario near Toronto. The ratios were used to differentiate STP-source materials from those coming from the nearby Humber River and the open lake. They found that $\delta\ ^{15}N$ values for sediment closest to the STP outfall, and thus most contaminated with sewage effluent, ranged from $+7.8^0/_{00}$ to $+4.9^0/_{00}$. These values are considerably higher than those mentioned above from marine studies (Sweeney and Kaplan, 1980b). Further investigation is needed to explain the discrepancy, but it could relate to differences in marine vs. freshwater nitrogen behaviour. $\delta\ ^{13}C$ ranged from -23.5‰ to -24.3‰ for samples closest to the outfall.

The above studies demonstrate that long-term fine sediment pathways can effectively be traced by analysis of the spatial concentration patterns of chemical components such as coprostanol and ratios of nitrogen and carbon present in the sediments. This is so despite the fact that these natural tracers are not fully conservative. Although confirmation must await core studies now in progress, it appears that such non-conservative effects are small compared to dilution and mixing.

DATA COLLECTION AND METHODS

Sample collection

In April, 1992, 30 bottom sediment samples were collected along a radial grid centred on the outfall of the Burlington STP (Figure 2). The goal was to collect undisturbed samples of

the topmost sediment layers, preferably using a corer. Because most sediments in the study area are very loose, they were difficult to collect using a corer, so an Ekman grab sampler was used. All samples were collected within a radius of approximately 2.5 km of the outfall. Sample depths were determined using a standard echo-sounder, and positioning was obtained by Mini-Ranger Falcon 484, an electronic positioning system. This line-of-sight system operates on microwave frequency, with a maximum range 40 km and an accuracy of 5 meters under ideal conditions.

To ensure that only the modern sediment layer was sampled, the sediment collected was limited to the top 2 cm. The grab sampler was carefully used to ensure that the surface was as undisturbed as possible. Before subsampling, careful description of the samples were made. Only if the samples showed indications of non-disturbed condition, such as a surface brown oxidized skin, were the top 2 cm collected.

Samples were put in dark glass bottles and stored in a cooler on the vessel during field work. On return to the laboratory, the samples were kept at 5° C prior to further preparation for analysis. Approximately 60% of each sample was freeze-dried. The freeze-dried samples were first homogenized, then split into four volumes used for different purposes:

- grain size analysis,
- organic content analysis,
- nitrogen and carbon stable isotope analyses,
- sample back-up or reference.

The remaining wet sample, approximately 40%, was returned to the sample bottles and then stored at 5° C prior to later use for coprostanol determination.

Coprostanol Analysis

Coprostanol was analyzed according to the method of Leenheer et al. (1984), with slight modifications (Telford et al., 1993; R. A. Bourbonniere, National Research Institute, Environment Canada, pers. comm. 1993). All solvents used were certified to contain no peak > 5 mg/ml as n-hexadecane by flame-ionization detector (FID). All reagents were analytical reagent grade or better, and all glassware was cleaned with detergent, water rinsing, methanol rinse, followed by dichloromethane rinse and oven drying at 60° C.

Soxhlet Extraction. About 5 g of dry sample or 10 g of wet sample were used. First, the unbound lipids in the sediment samples were extracted in a Soxhlet apparatus with 1:1.25 toluene:methanol for 24 hours, followed by an additional 24 hours extraction with 1:1 toluene:methanol. Heptadecanol (C17:OH) was added as an internal standard to the extract. Following this, the extract was partitioned. The first and second extracts were combined in a 1000 ml separatory funnel and partitioned with the aid of half-saturated NaCl at pH<1 (150 ml) to separate the unbound non-polar from the unbound polar fraction. Lipids remained in the organic (toluene) phase while the aqueous/methanol phase contains other polar compounds.

The aqueous/methanol phase was re-extracted twice with hexane (75 ml). The final aqueous/methanol phase was discarded. The organic (hexane) phases were combined with

their initial organic (toluene) phase and washed using half-saturated NaCl with pH < 1; afterwards the wash was discarded. The organic (hexane/toluene) phases were put in round-bottom flasks and evaporated to near dryness by rotary evaporation. Following this, the unbound non-polar fractions were saponified.

Saponification. The unbound non-polar fraction was dissolved with methanol:toluene 1:1 (2 ml, 3-4 times) in a 50 ml centrifuge tube and then saponified with 5 ml methanolic KOH (0.5 N KOH in 95% methanol, 5% H_20). The tube was placed in a boiling water bath for 20 minutes, then allowed to cool.

Methylation. The saponification is followed by methylation of the fatty acids with BF_3-methanol (14% w/w) and placed in boiling water bath for 5 minutes to produce fatty acid methyl esters (FAME).

Extraction. The methylation was followed by extraction with the aid of Milli-Q water (15 ml) and hexane (5 ml). The liquid levels of the different samples were balanced with Milli-Q water until all samples had the same liquid level. The tubes were centrifuged for a few minutes and the top organic phase was transferred into a 50 ml flask (50 ml) using a pipette. The aqueous /methanol layer was re-extracted two more times with hexane (5 ml). The aqueous/methanol phase was then discarded.

Column Chromatography. The lipids were fractionated into four fractions by chromatography in a column 9 mm in diameter packed with 2 g of aluminium oxide (Al_2O_3) over 2 g of silica gel. The lipids were evaporated just to dryness. Al_2O_3 (1 g) and FID DCM (10 ml) were added. Following evaporation to dryness, the sample, adsorbed to the alumina, was added to the column, and the column was eluted with four solvents:

- hexane/toluene (85:15) was used to elute hydrocarbons,
- toluene (100%) eluted FAME,
- ethyl-acetate/toluene (1:1) eluted hydroxy-lipids,
- DCM eluted the remaining fractions on the column.

The fractions were collected in 9.5 dram vials. All samples were stored refrigerated until Gas Chromatography (GC) analysis.

Sample Preparation for GC. The ethyl-acetate/toluene fractions were evaporated just to dryness, and later the samples were transferred to HP septum-capped vials using 2 x 0.5 ml heptane. BSTFA (Bis(trimethylsilyl)-trifluoroacetamide)(100 l) was added, and the samples were heated at 130° C for 15 minutes to make them more responsive on the GC capillary column. After cooled, the samples are ready for GC analysis.

Gas Chromatography. Analyses of coprostanol was carried on a Hewlett-Packard 5890A gas-liquid chromatograph with an on-column capillary inlet system, 30 m x 0.32 mm inside diameter fused silica column coated with DB-5 (J&W Scientific), and a standard flame-ionization detector (FID).

Coprostanol concentration was calculated based on relative response factor (RRF) from a reference solution containing 6.05 g coprostanol and 6.30 g reference standard (C18-

OH). Relative response factor (RRF) was determined using the following formula:

$$RRF = [\text{mg copros.(STD)} / \text{area copros.(STD)}] \times [\text{area C18-OH (STD)} / \text{mg C18-OH (STD)}] \quad (1)$$

From (1), coprostanol concentration in samples can be determined using the following formula:

$$\mu g \text{ coprostanol} = (RRF \times \text{area copros.} \times \mu g \text{ IS}) / [\text{area of internal standard (IS)}] \quad (2)$$

Stable isotope analyses

Stable isotope analyses were carried out by mass spectrometer (SIRA series II), which automatically measures the isotope ratio of a sample and then compares it with that of a standard. ^{15}N and ^{13}C on organic material are determined by converting the material into gaseous form, N_2 and CO_2 (LeBlanc 1989, Schwarcz and Schoeninger 1991). Freeze-dried sediment samples were first acidified with 1N HCl to remove any carbonates, then rinsed thoroughly with distilled water and dried overnight in an oven at 70° C. The dried samples were placed in 9 mm Pyrex tubes for nitrogen and 6 mm Pyrex tubes for carbon, to which was added an excess of cupric oxide (CuO). The tubes were evacuated and sealed with a flame, then combusted in a furnace at 550° C for 2 hours, and then slowly cooled. The resulting CO_2 and N_2 gas were purified by cryogenic distillation in a vacuum line and were introduced into the source of the mass spectrometer.

Stable isotope ratios were calculated in terms of X as follows:

$$\delta X = ((R_{(sample)} - R_{(STD)}) / R_{(STD)}) \times 1000$$

where X is ^{15}N or ^{13}C, and R is the ^{15}N / ^{14}N or ^{13}C / ^{12}C ratio, respectively. The standard for nitrogen was atmospheric N_2, $\delta\ ^{15}N = 0.0^0/_{00}$. Precision (1 standard deviation) for triplicate of organic standard (gelatine) when $\delta\ ^{15}N$ was analyzed is taken as $\pm 0.09^0/_{00}$. The standard used for carbon was PDB (PeeDee Belemnite carbonate). The $\delta\ ^{13}C$ error for triplicates of gelatine was $\pm\ 0.02^0/_{00}$. Precision of triplicate analyses of sample HH-STP was $\pm 0.123^0/_{00}$.

Grain size, organic carbon analysis

Grain size of sediment samples was determined using a combined Sieve/ SediGraph procedure (Duncan and Lahaie 1979). Organic content (%) was determined by first removing all carbonate, followed by sequential weighing after combustion at 550° C for one hour.

RESULTS

Table 1 shows the combined analytical results for the five sediment parameters around the Burlington STP outfall: coprostanol, nitrogen and carbon isotope ratios, organic content, and grain-size. Coprostanol concentrations averaged 43.0 $\mu g.g^{-1}$ and ranged from a maximum of 934.7 to less than 1 $\mu g.g^{-1}$. These values are an order of magnitude higher than

coprostanol values from Humber Bay near Toronto (Coakley et al., 1992), and from Chesapeake Bay (Brown and Wade, 1984).

The values of $\delta^{15}N$ range between +2.8‰ and +12.20‰ with an average +5.9‰, and for $\delta^{13}C$, the values range between -22.9‰ and -27.8‰ with an average -26.3‰. The ^{15}N values are of the same magnitude as those reported by Sweeney et al. (1980) and Cifuentes et al. (1988). The ^{15}N value right at the STP outfall (+2.8‰) is virtually identical with raw effluent ^{15}N values reported by Sweeney et al. (1980), i.e. +2.0‰ to +3.0‰. The ^{13}C value at the STP outfall (-22.9‰) shows the same magnitude as that reported by Cifuentes et al. (1988), i.e. -23.2‰ and Coakley et al. (1992), -23.5‰. The lowest values for ^{15}N and the highest (least negative) values for ^{13}C occur right at the STP outfall. These values increase and decrease, respectively, with distance from the outfall.

Organic matter concentrations ranged between less than 1 to almost 19%. Median grain size values ranged from 2.1 Ø (clean sand) in the onshore areas in the eastern part of the study area to 7.65 Ø (clay) in the deeper offshore areas. Fine sediments were also found close to shore in the lee of the concrete breakwater offshore of the Canada Centre for Inland Waters (CCIW).

Spatial distribution patterns of indicator properties

The spatial distribution of these values was examined by plotting their respective location positions on the sampling grid (Figure 2) followed by careful hand contouring. Net transport directions of each marker were then inferred based on the assumption that the source of indicator parameters was the Burlington STP outfall and that gradients extended from the STP outfall outward to background levels remote from the STP source. A similar approach was used by Coakley and Poulton (1991) and Coakley et al. (1992). This approach is qualitative and ignores differential erosion and deposition, and benthic processes such as bioturbation and chemical uptake and transformation. The method has been shown, however, to be effective in identifying net transport trends.

Coprostanol

As expected, the highest concentrations occur close to the outfall and decrease rapidly with the distance from the outfall. This trend is compatible with patterns associated with mixing / dilution (Holm and Windsor, 1984; Coakley et al., 1992), and confirms the STP outfall as the prime source. However, some samples close to the outfall (<400 m) had relatively low coprostanol concentrations, such as HH 4-2 (0.1 $\mu g.g^{-1}$), HH 6-2 (0.1 $\mu g.g^{-1}$), and HH 6-3 (0.0 $\mu g.g^{-1}$). This feature indicates that coprostanol values vary not only depending on the distance from the outfall (mixing and dilution), but also on other factors as well, as discussed in the next section.

The spatial distribution pattern for coprostanol (Figure 3) is markedly bi-directional with a main trend (high values) extending southward from the STP outfall and parallel to the east side of the Harbour. A secondary trend is directed toward the west, parallel to the north side of the Harbour, and curving southwest. An area of very low values was found in the area between these trends, i.e. within 500 m southwest of the outfall. South of this low, values

show a reversed gradient, with a slight increase toward the south.

Effect of organic content / grain size. In addition to mixing / dilution, two factors that might also be important in the distribution of coprostanol concentrations are sediment organic content (Hatcher and McGillivary 1979) and grain size. The latter is suggested by the consistently low values in the sandier areas (Table 1). The co-dependence of grain size with organic matter is well-known, as the low-density organic matter particles partition during settling with the fine-grained sediment fraction. Under these circumstances, normalizing coprostanol values against grain size (median phi diameter) or organic matter might enhance the coprostanol dispersion pattern.

As a first step, a linear regression was made of coprostanol on organic content and median grain size. The result for 27 samples, even when outlier samples with anomalously high concentrations (STP, 14-4, and 8-1) were excluded, was not significant ($R^2 = 0.08$). For grain size, the regression was even less significant, $R^2 = 0.02$, especially when compared with that for organic matter vs. median grain size ($R^2 = 0.85$). For this reason, no further attempt was made to normalize coprostanol against either organic matter or grain size.

This result suggests that coprostanol in Hamilton Harbour is not statistically associated with the organic fraction of the sediments, in contrast to the New York Bight studies (Hatcher and McGillivary 1979). Why this is so is not readily apparent. The STP outfall is clearly the predominant source for coprostanol in this section of the Harbour, and undoubtedly the coprostanol is discharged adsorbed onto organic particles (Brown and Wade, 1984). The most reasonable way to explain the lack of correlation between coprostanol and total organic matter in our study is by postulating that the total amount of organic matter discharged by the STP is very low compared to that from other sources in the Harbour (inflowing streams, primary productivity, etc.). In other words, the expected coprostanol signature of the STP-source organic matter is overprinted by a much larger input of organic matter from other sources. The idea of a supplementary source of organic matter for the study area, when viewed together with the reversing trend of coprostanol in the southern part of the sampling grid, lends support to the presence of other coprostanol sources in this part of the Harbour. One possible source that will be investigated further is the Hamilton STP (Figure 1) that discharges indirectly into Windemere Basin approximately 5 km south of the Burlington STP outfall.

Coprostanol is also not statistically associated with grain size, although it tends to be low in the sandier areas to the east. However, the fact that the fine-grained areas elsewhere show no correlation with higher coprostanol values is unexpected and deserves further investigation.

Nitrogen and Carbon Isotope ratios

The distribution of these indicators in the sediments is more uniform than that of coprostanol. The symmetrical pattern around the STP outfall indicates that the STP is an important source of light (^{15}N-depleted) nitrogen and heavy (^{13}C-enriched) carbon (Figure 4). The main trend inferred from the distribution of ^{15}N values is northward. A secondary trend is noted in the opposite direction, i.e. toward the south. Another minor trend is directly offshore and westward from the STP outfall.

Like the coprostanol pattern, an anomalous closed area of higher ^{15}N values occurs southwest of the outfall, and thence, the gradient is reversed. These trends support the results of coprostanol transport pattern which suggest the effect of a secondary source outside the study area.

The ^{13}C distribution is similar to the other indicators in that maximum (heaviest) values are centred on the STP outfall. However, the net trend is more symmetrical, with a main extension southeast from the STP outfall, i.e. more onshore than alongshore. Similar higher values (heavier) ^{13}C also occur in the inshore areas to the north. The implications of this divergence for the use of ^{13}C as a sediment tracer will be discussed later.

DISCUSSION

The spatial distributions of the sewage-source indicators, with the exception of ^{13}C allow us to draw conclusions on the pattern of fine sediment transport in the vicinity of the Burlington STP outfall. There is variation in the plumes delineated by coprostanol and ^{15}N, but the overall trends are clear. Coprostanol shows the clearest plume resolution, extending up to 2 km from the outfall. Because of the lack of a clear association of coprostanol with organic matter or grain size, normalization was not necessary, and the distribution of the values could be related primarily to dilution with distance from the outfall. However the reversal of the dilution gradient in the southern part of the grid suggests a relatively minor, or more distant, source of coprostanol to the south that deserves further investigation.

Although ^{15}N also is clearly associated with the STP outfall, and shows well-defined plumes, the resolution of these plumes remote from the outfall is much less than for coprostanol. This could be related to a number of factors, such as the addition of ammonia-nitrogen from metabolic processes in the sediments, isotopic fractionation, or the natural degradation of nitrogen in an oxidizing environment. Such factors could introduce trends unrelated to the STP discharge, and thus reduce the resolving capability of the tracer technique.

^{13}C shows a similar association with the outfall, but its plume diverges considerably in direction from that of the others. This divergence was not investigated closely here, but could indicate that Hamilton Harbour and the Burlington STP are not a closed system. The patterns suggest the presence of a number of secondary sources close to the STP outfall, and larger sources at a distance. In many cases, this causes some over-printing and reduction in the far-field resolution of the tracer techniques used. It is also possible that the ^{13}C fraction (particulate faeces) might be differentiated from the ^{15}N fraction (dissolved urine) in the effluent, and thus might be behaving differently in the transport process.

All of the above possibilities merit further investigation as they might limit the utility of ^{15}N and ^{13}C as sewage tracers in relatively restricted areas such as Hamilton Harbour, where there are potentially several sources of organic matter and nutrients. The role of mixing is therefore important and will be investigated further. Another area undergoing further study is the stability and persistence of coprostanol in oxidizing environments such as Hamilton Harbour.

Synthesis of net transport patterns from all indicators

Inferred net transport patterns deduced from plumes in coprostanol and ^{15}N ratios are shown in Figure 5. The dominant transport direction for sediments affected by the STP outfall is shown to be toward the south, parallel to the east side of the Harbour. A secondary trend is directed toward the north, curving toward the west along the north shore of the Harbour.

Overall, the main transport patterns appear to be shore parallel. No indication was evident of offshore transport to the deeper regions of the Harbour. This pattern suggests strongly that the effluent from the STP is being transported in the surface layers. Two factors support this conclusion:

- The temperature of the effluent is consistently higher than ambient temperatures in the Harbour, so the effluent plume would tend to be buoyant;

- The water depth at the STP outfall is less than 8 m, which indicates that stratification is minimal at the outfall site.

The shore-parallel sediment transport patterns inferred can be explained by wind-driven circulation within the boundary region of the Harbour. The prevalent wind climate, as indicated by the 5-year average from direction and speed data from just west of the Harbour is presented in Figure 5. Wind velocity was divided into 5 groups: 1-10, 11-20, 21-30, 31-40, and > 40 km/hour. The wind rose confirmed that the dominant wind direction was from southwest to northeast (32% of the record period), followed by northeast to southwest (19%), from west to east (18%), and northwest to southeast (16%).

Preliminary results from 2-dimensional (depth-averaged) circulation models of Hamilton Harbour show that the both main and secondary plumes from the STP outfall coincide in location zones of reduced flow (eddies) during northwest and west winds (Wu, 1993; I.K. Tsanis, McMaster University, pers. comm.). Elsewhere in the area, the model simulation indicated that during northwest and west winds, strong eastward currents are developed along the northeastern corner of the Harbour, which then follow the shore southward. These flows are capable of transporting fine sediments to the vicinity of the STP outfall. The secondary trend, i.e. toward the northwest and west, seems to be caused primarily by northeast winds that, according to the preliminary model simulation, would tend to produce a westward surface drift.

The use of a depth-averaged, 2-dimensional representation of circulation might be an oversimplification, and stratification might require some adjustment to this interpretation. At present, we have no data on stratification depths and times for this area of the Harbour. Furthermore, although the effluent is usually warmer (and less dense) than the surrounding waters, there might be times when the flow is much more turbid (i.e. under storm bypass conditions). The effluent plume might then be a sinking plume and follow the circulation of the hypolimnionic waters at depth. Further elaboration of these possibilities is beyond the scope of the present data base, but they demonstrate the need for investigation in greater depth before the tracer plumes can be more directly linked to the transport process. In any event, the net transport patterns identified by these plumes provide a useful first look at the long-term result

of innumerable transport / deposition cycles involving fine contaminated sediments associated with the Burlington Skyway STP.

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LIST OF ILLUSTRATIONS

TABLE 1. PERCENT CONTRIBUTION BY SOURCE OF SUSPENDED MATERIAL AND SELECTED CONTAMINANTS TO HAMILTON HARBOUR (Source: Canada - Ontario Agreement Review Board, 1992)

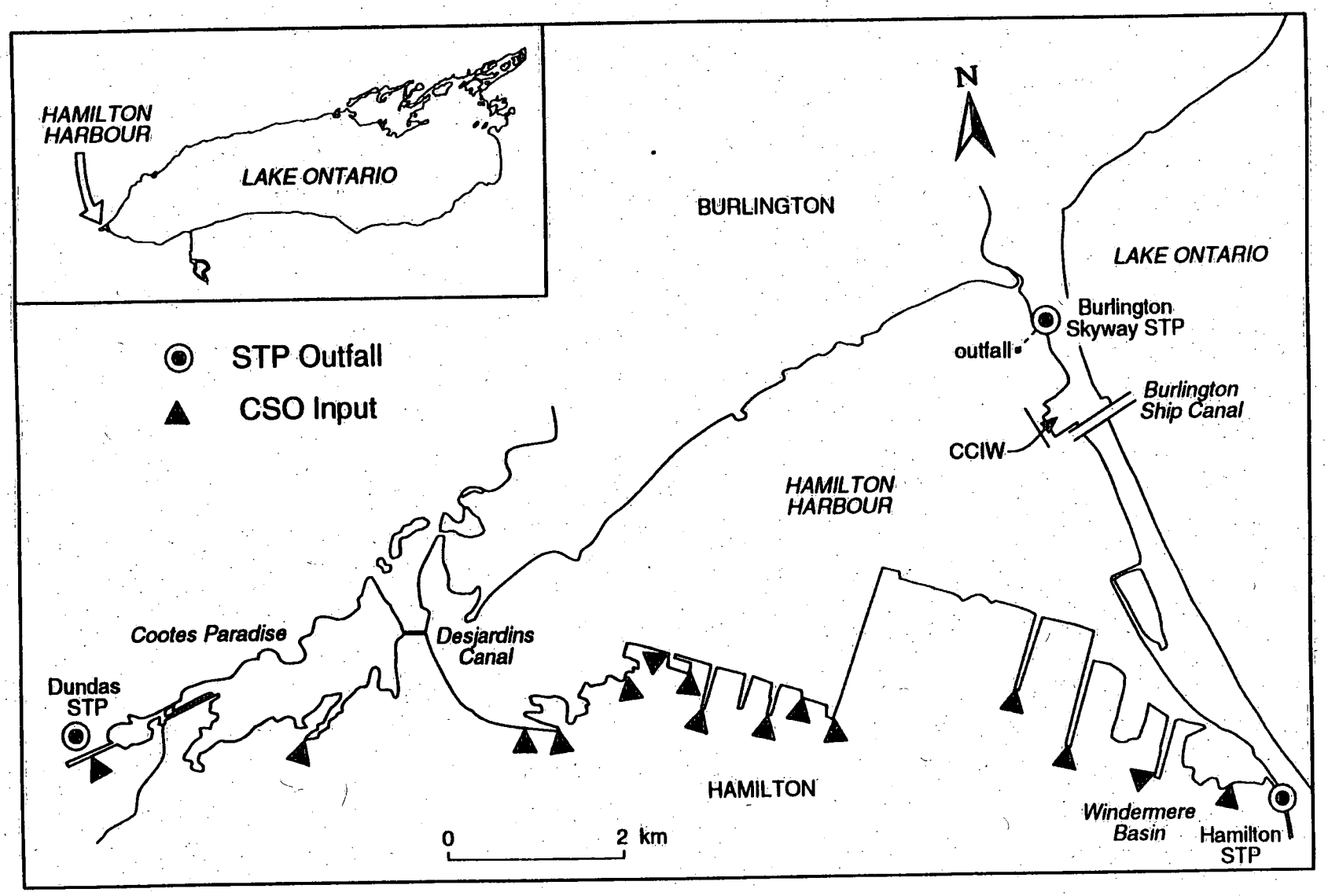
Source	Suspended solids	Zn	Pb	Fe	Cu	Cr
Burlington STP	**1.4**	**2.0**	**0.5**	**1.1**	**4.1**	**1.7**
All STP's	12.1	13.7	3.0	8.1	21.6	13.5
Cootes Paradise	28.5	5.1	12.9	13.8	9.8	6.3
Steel mills	18.8	53.3	6.4	56.3	9.9	19.7
CSO's	19.2	11.1	49.3	12.6	20.5	8.0
Streams & urban runoff	13.4	10.8	20.9	6.7	5.7	6.3
Lake Ontario	8.1	6.0	7.5	2.4	32.6	46.3
TOTAL LOADINGS (kg/d)	**44980**	**109**	**15.2**	**3156**	**14.1**	**31.8**

TABLE 2. ANALYTICAL RESULTS OF HAMILTON HARBOUR TRACER STUDY

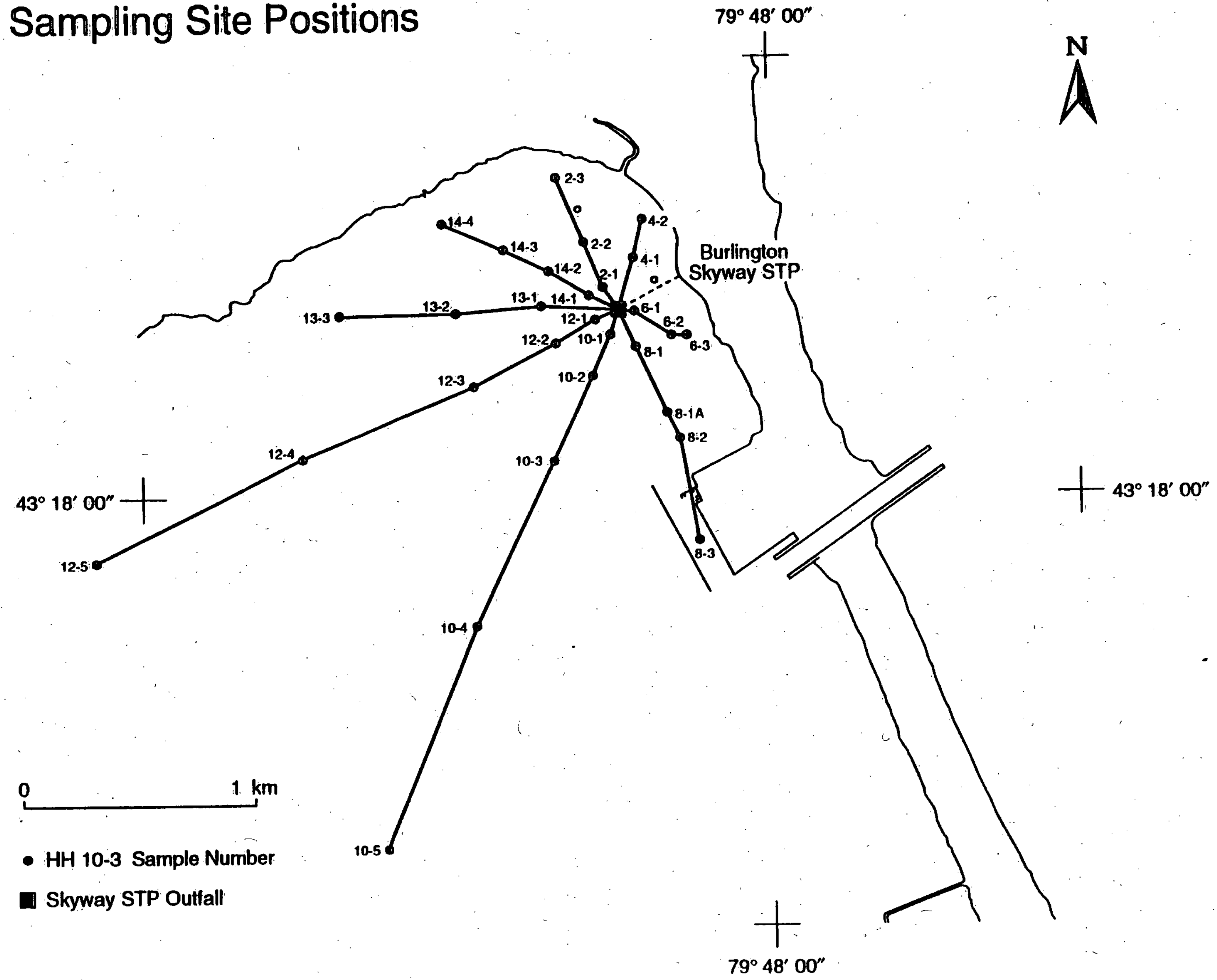
SAMPLE IDENT.	DIST. (m)	DEPTH (m)	COPRO. (µg/g)	$\delta^{15}N$ (per mil)	$\delta^{13}C$ (per mil)	MEDIAN (phi)	ORG. %
2-1	118	7.31	7.15	3.60	-25.70	5.26	4.50
2-2	320	3.81	1.56	3.50	-27.00	3.29	1.64
2-3	618	1.83	0.16	7.70	-26.50	3.26	0.77
4-1	218	2.41	2.88	5.90	-26.60	3.29	0.92
4-2	383	1.22	0.11	5.50	-26.50	2.71	1.02
6-1	59	4.88	37.13	3.90	-24.40	3.62	3.13
6-2	245	2.01	0.05	7.60	-25.30	2.25	0.57
6-3	306	1.37	0.04	9.40	-24.80	2.13	0.47
8-1	174	7.47	147.16	4.30	-24.90	6.42	12.96
8-1A	483	10.36	13.95	5.50	-26.40	5.86	6.79
8-2	603	5.03	0.50	6.30	-27.20	2.21	0.96
8-3	1041	9.14	9.31	6.00	-26.80	5.27	6.52
10-1	118	7.77	12.55	6.10	-24.90	6.83	17.91
10-2	314	6.09	0.34	6.80	-26.70	3.78	2.16
10-3	711	10.36	1.60	5.90	-26.80	6.29	9.42
10-4	1485	15.85	2.84	5.90	-27.50	7.42	12.34
10-5	2512	16.46	4.78	5.60	-27.70	7.36	15.25
12-1	124	8.38	46.90	4.10	-25.50	6.66	13.37
12-2	320	7.47	3.08	5.40	-26.80	3.94	4.29
12-3	723	12.34	0.82	5.90	-27.00	6.95	13.33
12-4	1532	16.61	3.23	6.10	-27.50	7.65	14.78
12-5	2531	19.61	2.67	5.90	-27.80	7.40	15.62
13-1	352	7.31	3.05	5.90	-26.90	4.34	4.48
13-2	718	10.06	14.61	6.50	-27.10	6.98	12.39
13-3	1226	9.01	4.41	6.50	-27.10	6.49	10.90

TABLE 2 (CONT'D). ANALYTICAL RESULTS OF HAMILTON HARBOUR TRACER STUDY

SAMPLE IDENT.	DIST. (m)	DEPTH (m)	COPRO. (µg/g)	$\delta^{15}N$ (per mil)	$\delta^{13}C$ (per mil)	MEDIAN (phi)	ORG. %
14-1	150	7.62	29.84	4.10	-26.10	3.31	9.23
14-2	356	6.25	1.52	5.70	-26.80	3.88	2.93
14-3	561	5.09	1.89	6.00	-27.40	3.95	2.55
14-4	849	2.44	0.18	12.20	-26.40	2.76	0.92
STP	0	6.86	934.75	2.80	-22.90	6.95	70.92


HAMILTON HARBOUR
LAKE ONTARIO
N
BURLINGTON
LAKE ONTARIO
STP Outfall
CSO Input
Burlington Skyway STP
outfall
Burlington Ship Canal
CCIW
HAMILTON HARBOUR
Cootes Paradise
Desjardins Canal
Dundas STP
HAMILTON
Windermere Basin
Hamilton STP
0
2 km

Sampling Site Positions



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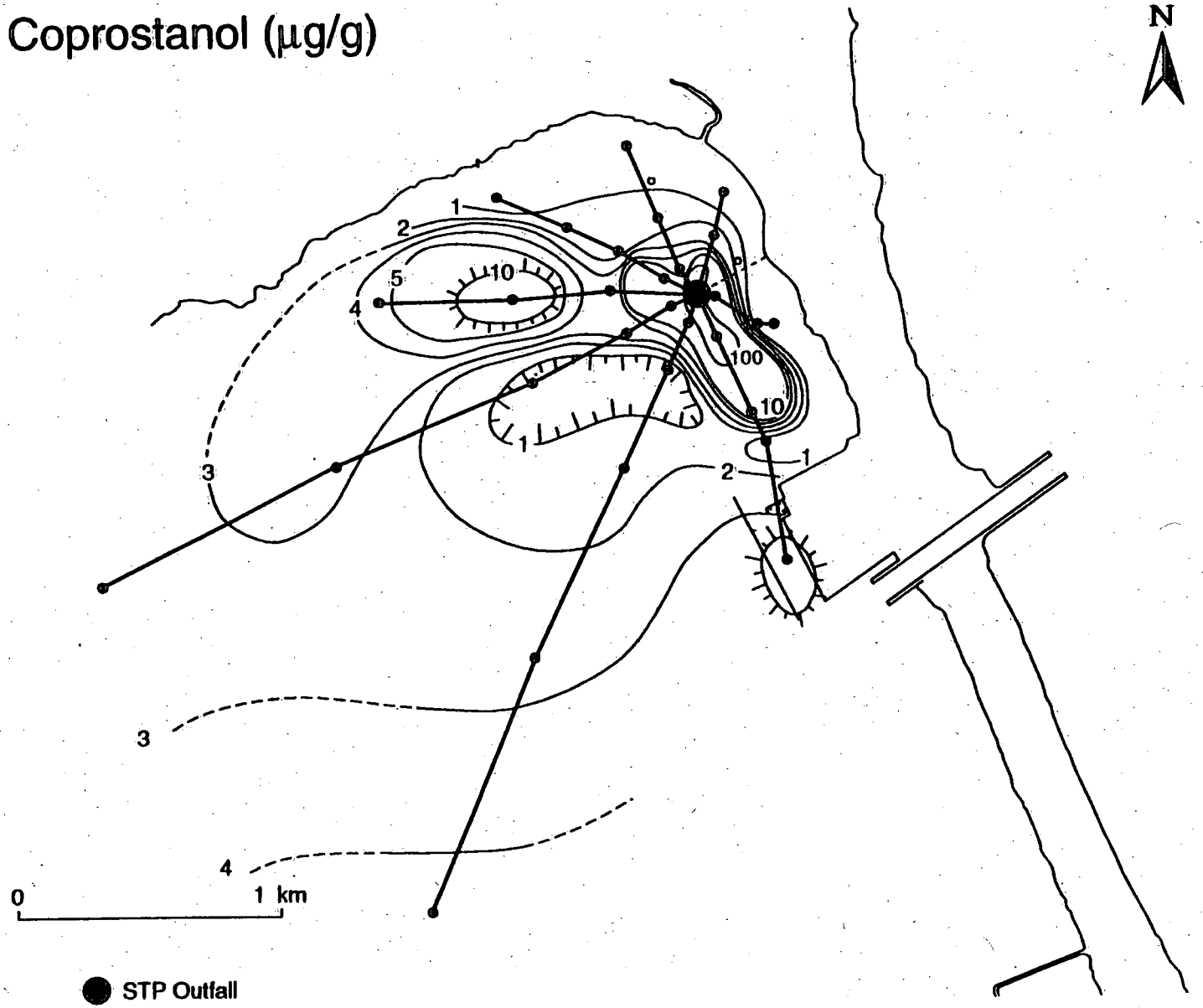
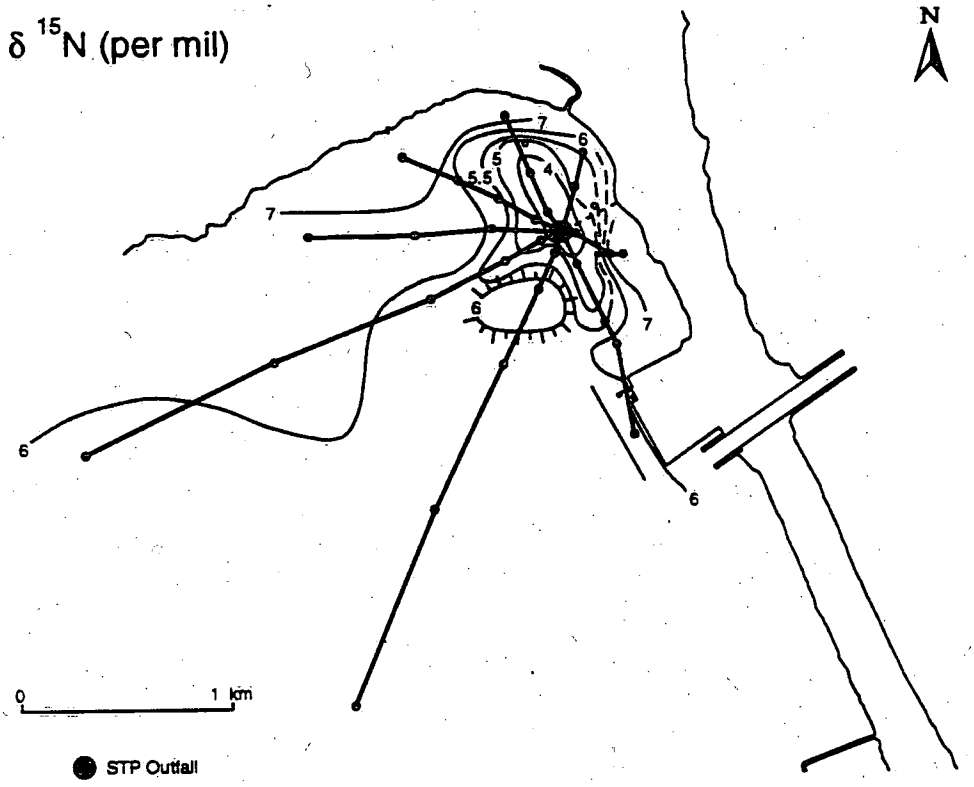
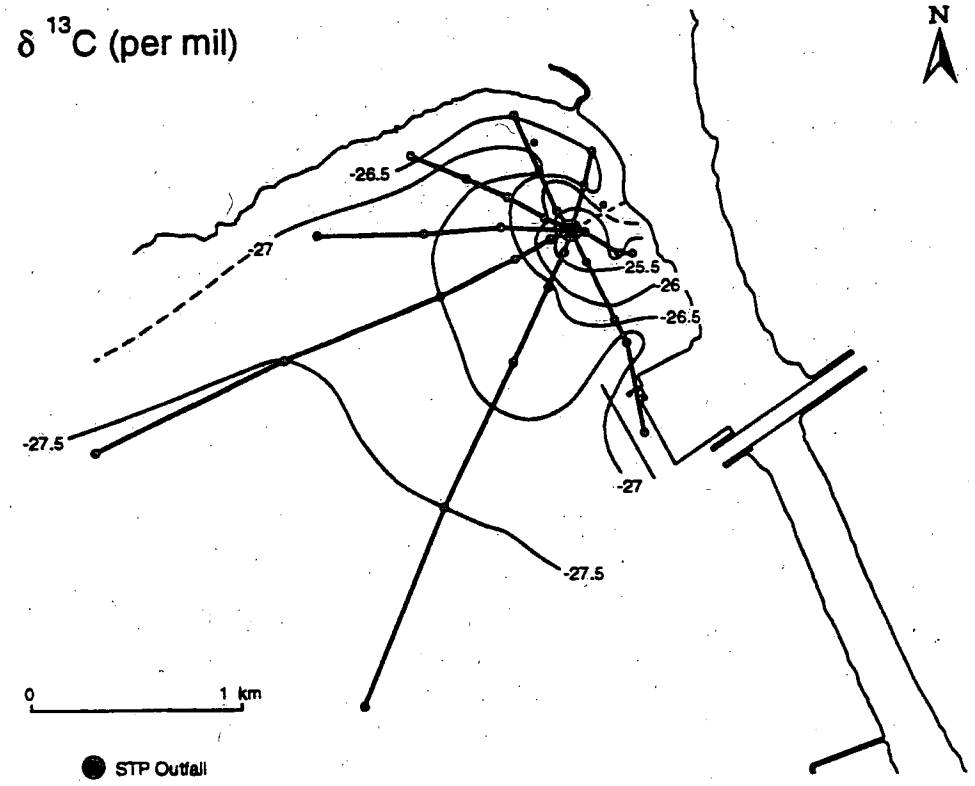
5


Coprostanol (µg/g)
N
1
2
5
10
4
100
10
1
3
2
1
3
4
0
1 km
STP Outfall





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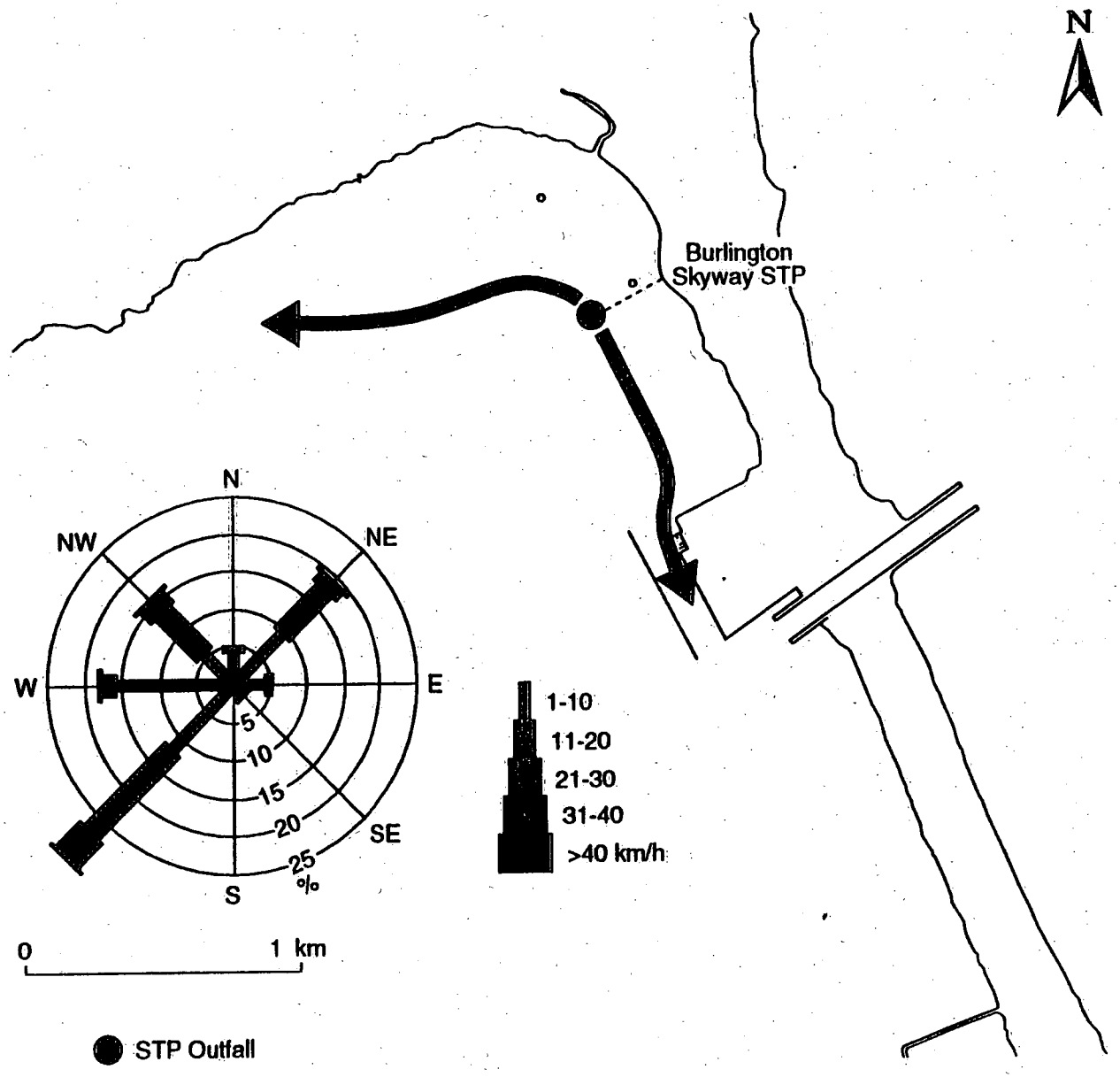
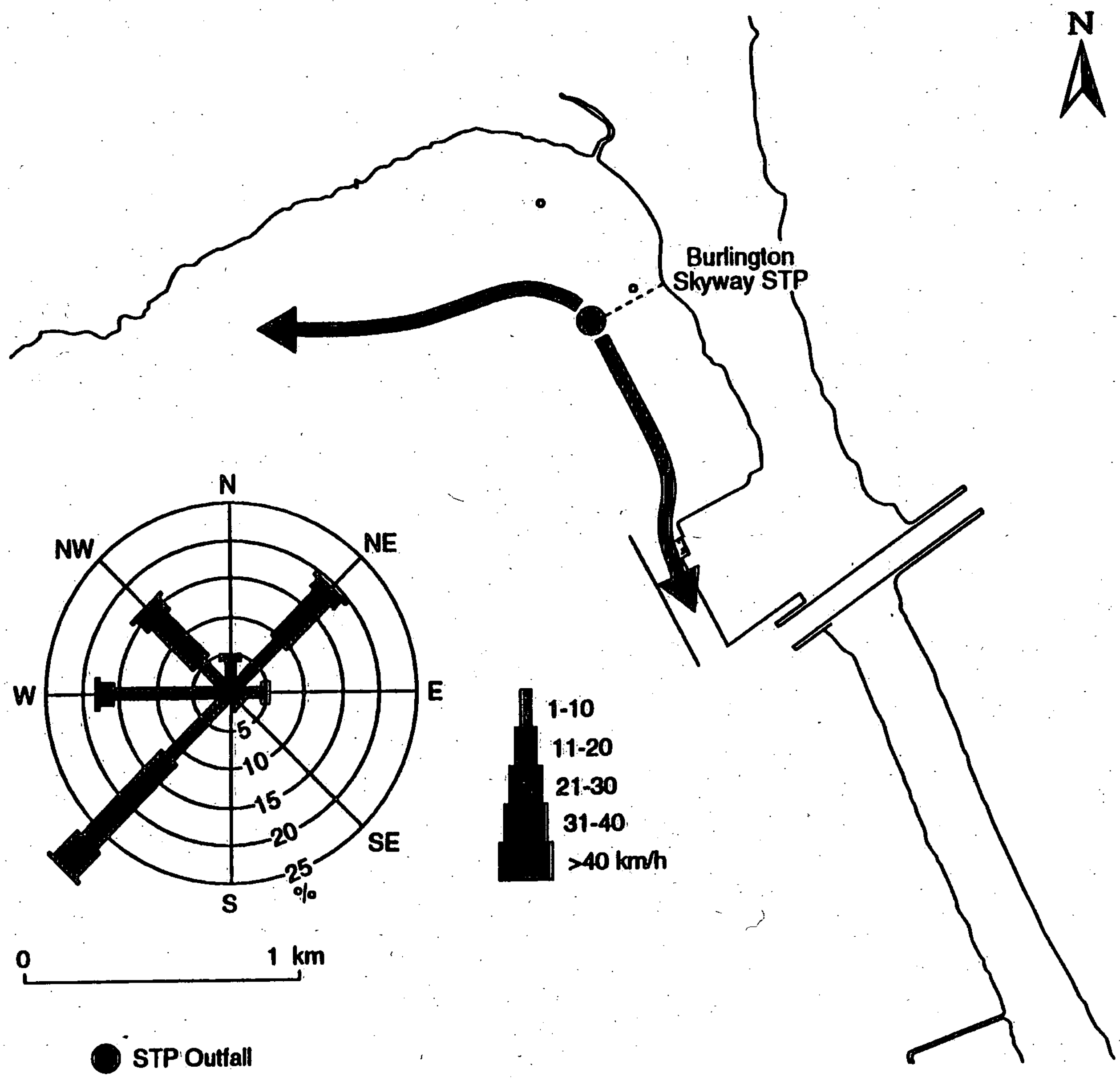
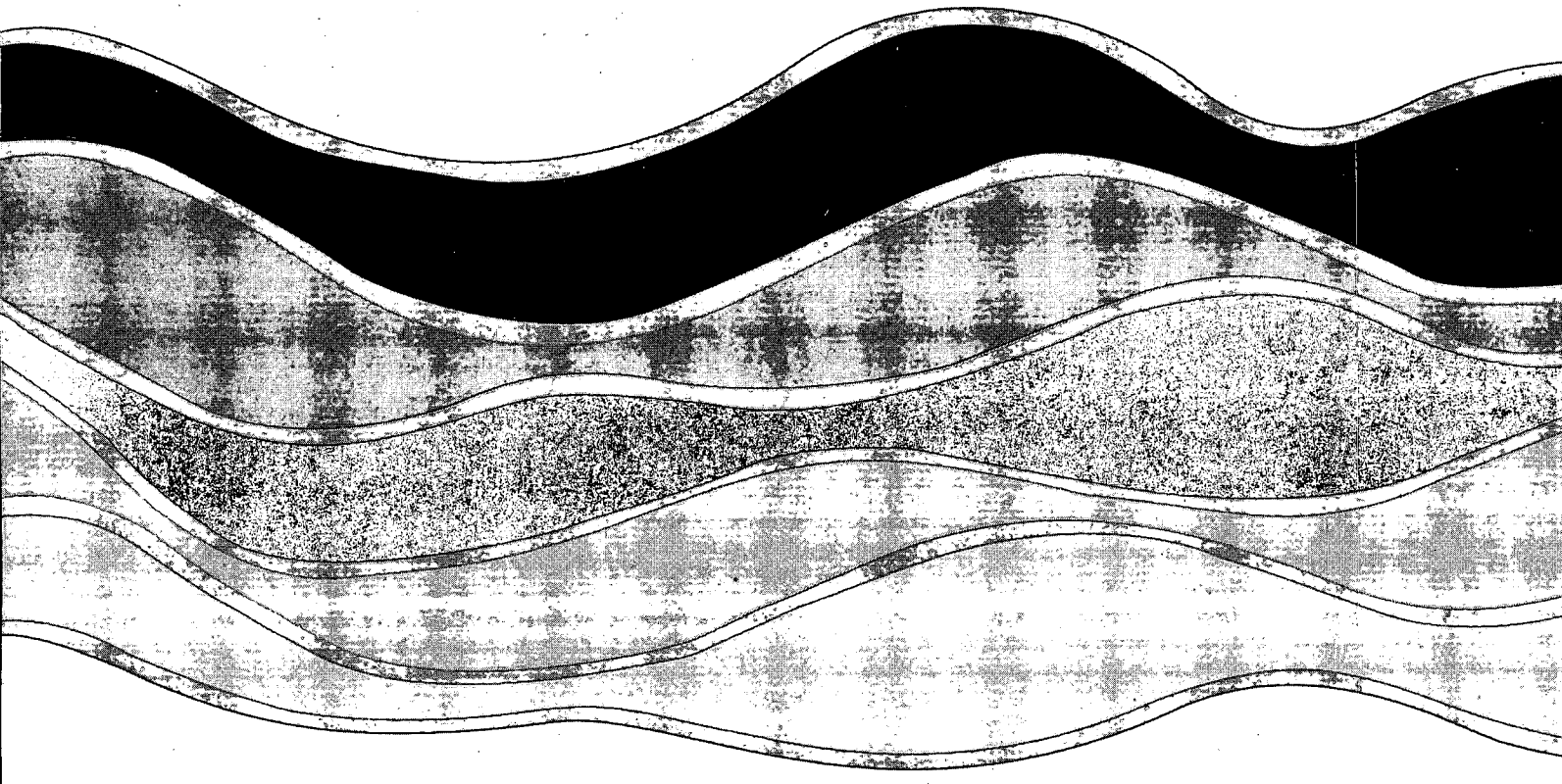

N
Burlington
Skyway STP
N
NW
NE
W
E
SE
S
5
10
15
20
25
%
1-10
11-20
21-30
31-40
>40 km/h
0
1 km
STP Outfall

(5)


N
Burlington
Skyway STP
N
NE
E
SE
S
W
NW
5
10
15
20
25
%
1-10
11-20
21-30
31-40
>40 km/h
0
1 km
STP Outfall

R7798



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