

Management Perspective

This report presents results of a 2-year intensive study of the nitrogen cycle in Hamilton Harbour conducted during 1987-88. Two components of the nitrogen cycle can have toxic effects on aquatic life. These are un-ionized ammonia and nitrite. Toxic un-ionized ammonia levels exceeded the International Joint Commission objectives (20 μ g/L NH₃-N) in all sampling sites for about half of the year (spring and summer). For extended periods in the late spring and mid-summer, they frequently exceeded acute toxic concentrations of 300-600 µg/L. Toxic ammonia concentrations were distributed unevenly and showed distinct areal zonation and patchiness. Volatilization of ammonia, estimated at 6.8 tonnes per season, is not a significant factor in overall NH3-N budget. The results suggest that the degree of toxic un-ionized ammonia contamination depends on total ammonia loadings from the municipal sewage treatment plants (Cities of Hamilton and Burlington) and that its formation is governed primarily by pH and water temperature conditions.

Nitrite concentrations were frequently above the IJC permissible limit of 30 μ g/L for most of the summer and often above acute toxic levels of 250 μ g/L (occasionally as high as 600-1,200 μ g/L near the outfall from the Hamilton sewage treatment plant). Under present conditions, nitrite is less frequently in the toxic range than un-ionized ammonia.

The report provides supporting information for the Hamilton Harbour RAP and demonstrates the need for further reduction of ammonia loadings from municipal sewage treatment plants in the basin, which will also solve the nitrite toxicity problem.

Perspective gestion

Dans de rapport, on présente les résultats d'une étude intensive de deux ans portant sur le cycle de l'azote dans le port de Hamilton en 1987-1988. On sait que deux composants du cycle de l'azote peuvent avoir des effets toxiques chez les organismes aguatiques. Il s'agit de l'ammoniac non ionisé et du nitrite. La concentration d'ammoniac non ionisé toxique a dépassé l'objectif de la Commission mixte internationale (20 ug/L, NH₃-N) dans tous les postes d'échantillonnage pendant à peu près la moitié de l'année (printemps et été). Pendant des périodes prolongées, à la fin du printemps et vers le milieu de l'été, les concentrations ont fréquemment dépassé la valeur de toxicité aiguë de 300 - 600 ug/L. La distribution des concentrations d'ammoniac toxique était inégale répartition et présentait une en zones et en plaques caractéristique. La volatilisation de l'ammoniac, estimée à 6,8 tonnes par saison, n'est pas un facteur important dans le bilan général du NH_a-N. D'après les résultats de l'étude, le degré de la contamination à l'ammoniac non ionisé toxique dépend de la charge totale en ammoniac des effluents des usines de traitement des eaux usées municipales (municipalités de Hamilton et de Burlington) et la formation de ce composé est essentiellement déterminée par la température et le pH de l'eau.

Les concentrations de nitrite ont fréquemment dépassé la limite admissible de la CMI, fixée à 30 ug/L, la plus grande partie de l'été et souvent, elles ont dépassé la valeur de toxicité aiguë de 250 ug/L (elles ont parfois atteint 600 - 1 200 ug/L près de l'exutoire de l'usine de traitement de Hamilton). Dans les conditions actuelles, la concentration de nitrite se trouve moins souvent dans la plage de toxicité que la concentration d'ammoniac non ionisé.

On donne des renseignements complémentaires concernant le Plan de mesures correctives du port de Hamilton et l'on démontre qu'il y aurait lieu de réduire encore davantage la charge d'ammoniac des effluents des usines de traitement des eaux usées du bassin hydrographique, ce qui aurait également pour effet de résoudre le problème de la toxicité due au nitrite.

ABSTRACT

The temporal and spatial distribution of total and toxic un-ionized ammonia, nitrite, nitrate and total dissolved nitrogen concentrations in Hamilton Harbour, Lake Ontario, were investigated during 1987-1988. The concentrations of toxic un-ionized ammonia in vertical and horizontal profiles depend on ammonia loadings from the Hamilton and Burlington municipal sewage treatment plants, the seasonal nitrogen cycle, pH and water temperature. Toxic ammonia levels in the Harbour exceeded the International Joint Commission objective of 20 μ g/L at all sampling sites for about half of the year (spring and summer). For extended periods in the late spring and mid-summer, concentrations frequently exceeded the chronic toxicity threshold of 300 µg/L. Toxic un-ionized ammonia concentrations were distributed unevenly over the Harbour with a distinct areal zonation and patchiness. Volatilization of ammonia, estimated at 6.8 tonnes per summer, reduced the toxic effect but was insignificant in the overall NH₃-N budget. The nitrite concentrations exceeded the chronic toxicity thresholds of 30 µg/L for most of the summer and frequently surpassed the cold-water fish toxic levels of 250 $\mu g/L$. Near the outfall from the Hamilton sewage treatment plant, nitrite levels were 600-1,200 µg/L. The frequency of nitrite toxic episodes was however lower than those of un-ionized ammonia. Nitrite was less abundant than total ammonia and can be considered as a less serious contaminant. Nitrification in Hamilton Harbour appeared to be inhibited by high toxic un-ionized ammonia levels.

RÉSUMÉ

En 1987-1988, on a étudié la distribution temporelle et spatiale des concentrations d'ammoniac non ionisé, de nitrite et de nitrate totaux toxiques et les teneurs en azote dissous total dans le port de Hamilton, dans le lac Ontario. Les concentrations d'ammoniac non ionisé toxique, en profils vertical et horizontal, dépendent de la charge en ammoniac des effluents des usines de traitement des eaux usées municipales de Hamilton et de Burlington, du cycle saisonnier de l'azote et du pH et de la température de Les concentrations d'ammoniac toxique dans le port ont l'eau. dépassé l'objectif de la Commission mixte internationale, fixé à 20 ug/L, dans tous les postes d'échantillonnage pendant à peu près la moitié de l'année (printemps et été). Pendant des périodes prolongées à la fin du printemps et vers le milieu de l'été, elles ont souvent dépassé le seuil de toxicité chronique de 300 ug/L. La distribution des concentrations d'ammoniac non ionisé toxique dans le port était inégale, présentant une répartition en zones et en plaques caractéristique. La volatilisation de l'ammoniac, estimée à 6,8 tonnes par été, a concouru à la réduction de l'effet toxique, mais elle était négligeable dans le bilan général du NH₂-N. Les concentrations de nitrite ont dépassé le seuil de toxicité chronique de 30 ug/L la plus grande partie de l'été et ont souvent été supérieures à la valeur de toxicité pour les poissons d'eau froide, soit 250 ug/L. Près de l'exutoire de l'usine de traitement de Hamilton, les concentrations de nitrite étaient de 600 - 1 200 ug/L. Les concentrations de nitrite ont toutefois atteint la valeur de toxicité moins souvent que les concentrations d'ammoniac non ionisé. Conne le nitrite s'est révélé moins abondant que l'ammoniac total, on peut considérer ce polluant comme étant moins dangereux. Il semble que dans le port de Hamilton, la forte concentration d'ammoniac non ionisé toxique inhibe la nitrification.

INTRODUCTION

Of the nitrogen forms normally present in natural waters, ammonia is often the major pollutant, presenting a potential toxic threat to aquatic organisms (U.S. EPA 1985). Because of the high residential and industrial density, ammonia, discharged in treated municipal and industrial effluents, is the major foreign component in Hamilton Harbour (MOE 1981, 1985). The diluting and self-purifying capacities of the Harbour are inadequate to accommodate the effluents by natural processes (algal uptake, bacterial nitrification). Total ammonia levels remain at mg/L levels for most of the year and, under certain ΰĤ and temperature conditions, pose a direct toxic threat to aquatic The toxicity of aqueous ammonia solutions to aquatic life is organisms. primarily attributable to the un-ionized NH₃ species. The ionized NH4+ species is considered to be non-toxic (Trussel 1972, Emerson et al., 1975). Concentrations of un-ionized NH₃ should not exceed 20 µg/L for the protection of aquatic life (IJC 1978, U.S. EPA 1985). Lethal concentrations (LC_{50}) range from 200 to over 2000 μ g/L with salmonids being the most sensitive and species, the warm-water least. The generally accepted minimum LC₅₀ concentrations of un-ionized NH₃ are 200-300 μ g/L (EIFAC 1970).

Nitrite is an intermediate product of either the nitrification of ammonia or the denitrification of nitrate. Although nitrite is toxic to aquatic (as well as human) life, there is no IJC objective for NO_2 -N. However, Russo <u>et al</u>. (1974), Wedemeyer and Yasutake (1978), Thurston <u>et al</u>. (1978), and C.C.R.E.M. (1987) suggest chronic toxicity levels thresholds between 15-60 µg/L (on average 30) for both trout and carp. Acute toxicity levels start at 240 µg/L for trout (Lewis and Morris, 1986).

-3-

Hamilton Harbour offered a unique opportunity to study temporal and spatial variations of both ammonia and nitrite, together with other related parameters, and to analyze limnological conditions in an aquatic system overloaded with treated effluents. This paper presents the results of field studies conducted during 1987-1988. Information is presented on the ammonia speciation during seasonal cycles, the duration of toxic periods, areal "patchiness" and ammonia volatilization. The paper also contains information on nitrite and nitrate regime and nitrite toxic events.

STUDY AREA

Hydrology and water quality

Hamilton Harbour, an embayment of Lake Ontario, contains about 2.8x10⁸ m^3 of water. It has a surface area of 21.5 km², maximum depth of 23 m, and mean depth of 13 m. The harbour is contaminated by industries on the highly developed south shore, which use 27 m^3/s of water and return a similar amount of effluent to the harbour (MOE 1981). The harbour also receives 4.3 m^3s^{-1} of treated wastes from municipal utilities, tributary flows, and 3.5m³s⁻¹ of stormwater runoff. Concentrations of ammonia, zinc, total untreated phosphorus, iron, phenols, cyanide, copper, nickel, chromium, the coliforms and the turbidity levels exceeded the provincial water quality objectives in 1983 (MOE 1985). Loadings of phosphorus and nitrogen in 1985 were 609 kg/day and 7,076 kg/day respectively, resulting in concentration ranges of total P of 40-200 µg/L and ammonia of 100- >10,000 µg/L (as N). Nutrient loadings cause severe harbour eutrophication (Haffner et al. 1980) and hypolimnetic dissolved

-4-

oxygen depletion (Polak and Haffner 1978). Deterioration of water quality, exploitation and competition contributed jointly to the large-scale decline of the cold water fish community of Hamilton Harbour (Holmes and Whillans 1984). Because of poor water quality, Hamilton Harbour was designated by U.S.-Canada International Joint Commission as one of 42 areas of concern in the Great Lakes basin. A remedial action plan is underway (DOE-MOE 1989).

Hamilton Harbour is separated from the main water body of Lake Ontario by a ship canal, which cuts through the sandbar at the eastern boundary of what was originally a natural embayment with limited water exchange. The exchange of water between Lake Ontario and Hamilton Harbour through the canal (840 m long, 107 m wide and 9.5 m deep) is a complex dynamic process, bringing large amounts of oligotrophic Lake Ontario water into the Harbour.

Ammonia loadings

Total ammonia loadings from various sources in Hamilton Harbour were estimated to be 7500 kg/day (DOE-MOE 1989). The Hamilton sewage treatment plant (STP), serving a population of 300,000, discharged 5,300 kg/day in 1987, or about 70% of the total loading. The Burlington STP, serving a population of 120,000, represented the second largest source of ammonia discharged to the Harbour, with a loading of 1150 kg/day in 1987 (15% of the total loading). Additional large sources of ammonia were the steel industries: Stelco with 627 kg/day or 8%, and Dofasco with 244 kg/day or 3% of the total). Combined sewer overflows (CSOs) were estimated to contribute 200 kg/day (3%) in 1987.

-5-

Total ammonia loadings to Hamilton Harbour have significantly decreased since the late 70's and early 80's, where major reductions were achieved in the steel industry. Ammonia loadings decreased from 24,000 kg/day in 1967 to 857 kg/day in 1987. Further reductions are scheduled in the next few years. Loading reduction from the municipal STPs were less noticeable. Improvements are expected under the remedial action plan (DOE-MOE 1989) through introduction of nitrification stage during sewage treatment.

SAMPLING SITES AND METHODS

Study sites

A total of 35 cruises were conducted during 1987-1988. Water samples were collected at 5m intervals. Measurements included turbidity, conductivity, water temperature and dissolved oxygen profile (YSI meter and/or Winkler method) as well as pH readings and Secchi disc profiles.

Water quality parameters for seasonal and vertical variability were measured at six main stations in the harbour between February 10, 1987 to September 13, 1988 in intervals ranging from one week to two months, depending on accessibility due to ice conditions in the winter. Sampling frequency during 1987 was generally higher than during late 1988. In addition, areal distribution was measured monthly at 38 additional stations in the Harbour and near the ship canal to Lake Ontario (Fig. 1).

Methods

Water samples were filtered immediately after collection through a 0.45 um cellulose acetate filter and analyzed at the National Water Quality Laboratory. Total dissolved (filtered) nitrogen (TDN-N) was determined by an autoclave method using sulfate oxidation of nitrogen to nitrate. Nitrate plus nitrite were determined together after reduction through a coil containing cadmium filings to reduce nitrates present to nitrites. Nitrites were reacted with sulfanilamide to form the diazo-compound. Total ammonia was determined after reaction with alkaline phenol hypochlorite to form indophenol blue. Chlorophyll <u>a</u> was determined on GF/F filters fluorometrically after acetone reduction. Additional details can be found in National Water Quality Laboratory analytical manuals.

Canal currents were measured on seventeen occasions. Phytoplankton samples and phosphorus data collected during the study have been presented separately elsewhere (Barica and Vieira, 1988).

Equilibria

<u>Calculation of un-ionized ammonia</u>: Dissolved ammonia equilibrates between the ionized (NH4+) and the molecular un-ionized (NH₃) form with the latter being about two orders of magnitude more toxic to fish (Emerson <u>et al</u>. 1975). The percent of un-ionized ammonia in an aqueous ammonia solution increases as the pH increases according to the following equilibria:

$$NH_4^+ + OH^- \langle ---- \rangle NH_3$$
. $H_2O \langle ---- \rangle NH_3 + H_2O$

Corresponding ionization constants for this equilibrium are:

$$K_{i} \text{ (ammonia)} = \frac{(NH4) \times (OH)}{(NH_{3})}$$

$$K_{\omega}$$
 (water) = (H) x (OH)

Both K_i and K_w change with temperature. The equilibrium between NH_3 and NH_4^+ shifts toward NH_3 formation as the temperature increases. The combined influence of pH and temperature on the fraction of total ammonia in the un-ionized form (NH_3) has been described and tabulated by Trussel (1972) and Emerson et al. (1975) according to the following equation:

Fraction of Total Ammonia = $\frac{1}{1 + 10^{(pKa-pH)}}$ (1) in un-ionized Form (NH₃) $1 + 10^{(pKa-pH)}$

where pKa = 0.09 + -2730273 + T

and $T = {}^{\circ}C$

-8-

The presence of dissolved solids will lower the concentration of un-ionized ammonia slightly. In the Great Lakes waters, the magnitude of this effect will usually be less than that of changing the temperature by 1 °C under otherwise constant conditions. The influence of dissolved solids was therefore ignored. Toxic un-ionized ammonia (termed here as toxic NH_3-N) results were calculated from total ammonia concentrations, pH and temperature readings at each sampling depth, using Trussel's 1972 table between 5-25 °C and pH 6.5-9.0 and Emerson's et al. (1975) tables for pH over 9.0.

genera of bacteria, Nitrobacter Nitrite-Nitrate equilibria: Two and Nitrosomomas are involved in the two-step conversion of ammonium to nitrate (nitrification). Different factors may affect species of these two genera and result in the accumulation of nitrite. Nitrobacter spp., which convert nitrite to nitrate, are more sensitive to un-ionized ammonia than are Nitrosomonas spp. which convert ammonium to nitrite (Lewis et al. 1986). The overall equilibrium between nitrite, nitrate and ammonia is controlled by either nitrification or denitrification processes (Rodina 1972). Levels of nitrite nitrogen are typically less than 5 μ g/L in unpolluted natural waters (U.S. EPA 1985). Under some circumstances, the concentrations of nitrite may be high enough to alter hemoglobin and thus be toxic to aquatic organisms.

RESULTS

Seasonal variability and cycles of nitrogen compounds and related water quality parameters.

-9-

Figures 2 and 3 present averages for concentrations of total and toxic ammonia; nitrate, nitrite, and total dissolved N; pH, water temperature, dissolved oxygen and chlorophyll <u>a</u> for the top 10 m, i.e., the approximate thickness of the epilimnion at the centre of the Harbour when stratified. All six sampling sites for vertical profiles are combined for convenience into two groups:

1. Figure 2 represents data from sites directly affected by sewage treatment plant (STP) outfalls from Hamilton (Sites 1 and 2) and Burlington (Site 6).

2. Fig. 3 represents sites distant from the STP outfalls (Sites 4 and 5 and Site 3 near the ship canal; i.e. sites where natural Hamilton Harbour water is unaffected directly by sewage effluents). Site 3 is occasionally affected strongly by Lake Ontario water exchange depending on flow conditions in the canal (MOE 1986, Barica et al. 1988).

Data base for all discrete sampling depths as well as hypolimnetic conditions are available elsewhere (Barica and Vieira 1988).

<u>Nitrogen Cycle</u>: Due to effluent loadings of about 7,000 kg per day of ammonia; (DOE-MOE 1989) from the two sewage treatment plants discharging into the Bay, the distribution of nitrogen forms displayed in Figs. 2-3 is not uniform in either temporal or spatial terms. Consequently, concentrations range widely: ammonia $(0.1->10 \text{ mg/L NH}_3-\text{N})$, nitrate $(<1-2.5 \text{ mg/L NO}_3-\text{N})$ nitrite $(0.01->0.2 \text{ mg/L NO}_2-\text{N})$ and total dissolved nitrogen (1.9->10 mg/L TDN-N). Ammonia is the major contaminant in the Harbour. Conditions for its dissociation into NH4⁺ ion and toxic NH₃ gas prevail during the warm months of the year (May-September).

-10-

Sampling sites Nos. 4 and 5 (Fig. 3) appear to be least affected by the concentration fluctuations caused by the discharge of effluents from both sewage treatment plants or dilution caused by the intrusion of Lake Ontario water through the canal (site 3). These sites, therefore, provide the most representative models of seasonal cycles in inorganic N-parameters.

Total ammonia N, the major form of nitrogen in the harbour, displays a distinct seasonal cycle with maximum values of 1.4-1.7 mg/L NH_3 -N) occurring in the winter. These maxima persist until April-May. From June on, maximum total ammonia concentrations decline at an approximate rate of 0.5 mg/L per month. By mid-July, total ammonia concentrations reach values of about 0.2-0.3 mg/L and continue to decrease at a slower rate (<0.1 mg/L/month) until minimum levels <0.1 mg/L are achieved in November. From then on, ammonia levels increase to maximum values of over 1.5 mg/L in March (Site 5). Site 6 shows a similar trend with NH₃ concentrations about 30% higher due to the ammonia input from Cootes Paradise, a shallow eutrophic extension of Hamilton Harbour (Fig. 1). N-cycle at Site 3 appears to be significantly disrupted by Lake Ontario water intrusions.

As a result of elevated water temperature and pH values, significant dissociation of total ammonia into NH_4^+ ion and toxic un-ionized NH_3 gas starts as early as April with NH_3 levels in excess of 20 µg/L, the objective set by the IJC. By early May, the levels of un-ionized toxic ammonia rise dramatically and for a period of 1-2 weeks exceed LC_{50} levels of 300 µg/L (U.S. EPA 1985). Permissible levels continue to be exceeded for most of the summer. By October, un-ionized ammonia concentrations drop again below the 20 µg/L limit and remain there throughout the winter months.

1

-11-

The gradual loss of ammonia from the water column with the advancing warm season can be explained by algal uptake, bacterial nitrification, volatilization and physical exchange. All of these processes appear to be However, the nitrate concentrations during this operating simultaneously. period do not increase proportionally as NH3 decreases, as it would be expected stoichiometrically in oxygenated water. Nitrate concentrations continue falling rather than increasing gradually during the warming period and follow the ammonia trend for some time. Nitrate concentrations decrease from over 2.0 mg/L NO3-N in February to 1.6-1.8 mg/L in April-June. They continue to fall and by September they reach their minima of 1.3-1.4 mg/L Then, NO,-N concentrations start to rise again, reaching the seasonal NO₃-N. maximum of about 2.0 mg/L NO₃-N by December. While temporal changes in NO₃-N concentrations are not as substantial as those of ammonia, their vertical distribution was more pronounced (Barica and Vieira 1988). During June, the lower than epilimnetic hypolimnetic concentrations are 20-30% levels. suggesting intensive denitrification processes in the hypolimnion (Klapwijk and Snodgrass 1982).

Throughout the annual cycle, nitrite concentrations are lower than $NH_3 = N$ and $NO_3 - N$ (mostly under 100 µg/L $NO_2 - N$) and clearly respond to the ammonia cycle. Nitrite is present at low concentrations during the winter months (30-70 µg/L $NO_2 - N$), but frequently exceeds chronic toxicity guidelines. It then increases proportionately with the ammonia decrease to about 240 µg/L and over in September, when total ammonia depletion begins and peak of nitrification occurs. These levels may be acutely toxic to some fish species (Lewis and Morris, 1986). Nitrite decreases again to below 20 µg/L in early October, together with disappearing total ammonia, and remains low for the rest of the season.

Total dissolved (filtered) nitrogen (TDN), i.e., the sum of NH_3-N , NO_2-N , and NO_3-N and the dissolved organic nitrogen concentrations, represents the total pool of dissolved N. Maximum TDN concentration (about 3.8 - 4.1 mg/L) occur in winter and spring months, but decrease to an average of 2.0 mg/L and less in mid-summer. This substantial reduction of 1.8-2.1 mg/L N corresponds roughly to the loss of ammonia, suggesting that the cause may be volatilization rather than sole conversion to NO_3-N through nitrification.

sites affected directly by effluent distribution in Nitrogen discharges (site Nos. 1, 2, and 6; Fig. 2) is governed more by these discharges than by seasonal cycles. Sites 1 and 2 (inflow from the Windermere Basin and the Windermere Arm) show total ammonia levels of over 10 or 5 mg/L respectively, and represent the section of the Harbour with the highest ammonia loadings. However, because effluent discharges depress pH levels by about 1 pH in comparison to the rest of the Harbour, the concentration and frequency of occurrence of toxic un-ionized ammonia at these sites are not significantly higher than in the main body of the Harbour. Although this part of the Harbour is thermally unstratified, high ammonia concentrations appear always near the surface, in the warmer water entering from the Windermere Basin (Barica and Vieira, 1988). NO3-N concentrations there are generally lower than in the main lake, while NO2-N is higher, indicating denitrification in the Windermere arm. Site 6, near the outfall from Burlington STP, presents less pronounced N-fluctuations as loadings from the Burlington STP are about 10-20% of those from the Hamilton STP.

Site 3 - near the Ship Canal - showed extreme fluctuations of all parameters and a poor seasonal cycle, as it is governed by water exchanges with Lake Ontario. Regular intrusions of unpolluted water improve water quality of the Harbour by about 30% (Barica 1989).

-13-

<u>Chlorophyll and other parameters</u>: Chlorophyll <u>a</u> values in Hamilton Harbour approached the algal bloom conditions. Occasional surface maxima are 20-30 μ g/L chlorophyll <u>a</u> with corresponding Secchi disc transparencies of <1 m. pH fluctuated significantly between values over 9 at the surface during summer, to less than 7 during the winter and spring, enabling development of un-ionized toxic NH₃ and at the same time its volatilization.

Dissolved oxygen conditions, which are the subject of a separate study (M. Charlton, in preparation), are generally saturated in the epilimnion but become severely depleted (<1.0 mg/L) in the hypolimnion in the late summer (Barica and Vieira 1988).

Vertical distribution: Fig. 4 presents the four characteristic stages of vertical distribution of selected parameters occurring during early-to-midsummer in the deepest spot of Hamilton Harbour (Site 5; 23 m deep). In the winter and early spring, the concentrations of total ammonia and other nitrogen forms are more or less uniform throughout the profile. Distinct thermal stratification is noticeable by mid-June. In the later part of the summer, the vertical distribution profile reverses itself, with the nitrogen This reverse pattern minima occurring near both the surface and the bottom. prevails until the end of the summer (late September - early October). After the fall turnover, a uniform minimum concentration throughout the water column All total ammonia appears to be depleted, presumably is again reached. algal uptake, nitrification, volatilization and physical water through For the rest of the winter season, vertical distribution remains exchange. throughout the whole profile due to the absence of thermal uniform stratification.

-14-

Unlike total ammonia. toxic un-ionized ammonia does not show this reversal of vertical distribution. Concentrations of un-ionized ammonia always occur in the top 5 meters of the surface water. By June 18, thermal stratification was well developed, but its impact was obvious only on chlorophyll a and dissolved oxygen profiles. The nitrogen forms were governed primarily by loadings and their vertical distribution was only partial, particularly that of total ammonia, was not clearly developed and appeared to be unaffected by thermal stratification as evidenced by the almost straight vertical lines of total NH₃. While the trends discussed in the previous section are noticeable throughout the whole vertical profile (a general decrease of total NH₃ and TDN and increase of NO_3 and NO_2-N over the summer period), the formation and vertical distribution of toxic un-ionized ammonia appears to be governed primarily by pH. On May 11, 1987, for instance, the top 5 m layer contained 250-591 μ g/L of toxic NH₃-N at the surface which is near and well above the LC_{50} for trout (300 µg/L). This acutely toxic layer persisted for less than a week without causing any obvious damage to fish populations in the Harbour. Abnormally high concentrations of toxic NH₃-N were caused by anomalous high pH values in the surface 5 m layer (9-9.8), likely caused by discharges of alkaline effluent and perhaps by increased uptake of CO₂ by spring bloom of Chrysophytes and Chlorophytes which was then underway (Barica and Vieira 1988).

In the following period, toxic NH_3 -N levels fell to between 50-100 μ g/L, i.e. still above the IJC objective of 20-30 μ g/L. This applied only to the top 10 m (epilimnion); hypolimnetic concentrations did not show any pronounced variability.

It is noteworthy that during summer stratification, all NO_3-N , NO_2-N and TDN concentrations gradually decline with the sampling depths below 5 m. The surface layer, however, shows a significant drop in concentrations between 5 m and the surface, which again suggests a loss of nitrogen from the surface through volatilization.

Loss of ammonia through volatilization

In the previous sections, the discrepancies between stoichiometry of different forms of nitrogen, their transformations and the seasonal cycles in oxygenated epilimnion have been assumed to be due to the loss of un-ionized ammonia from the water surface. This process is also apparent from the vertical distribution of N-compounds (Fig.4).

Due to extremely high loadings, nitrogen is certainly not a phytoplankton limiting nutrient in Hamilton Harbour. Therefore, vertical distribution of its dissolved species in the epilimnion is not governed primarily by phytoplankton uptake as expected in unpolluted lakes. Accordingly, the vertical distribution of total ammonia are therefore fairly uniform, and the most frequent distribution is either a straight line or a right-turn curve:

With the progressing summer season, the right turn curve becomes more predominant, suggesting an accumulation of excessive ammonia from the lower

-16-

epilimnetic layers of the lake by biological or physical processes. For certain periods, the vertical distribution curves become reversed (left-turn):

The above distribution suggests the loss of ammonia (both total and toxic) from the top water layer. Considering the fact that the chlorophyll a levels during these periods remain almost constant, and primary production is generally inhibited in Hamilton Harbour (Haffner <u>et al</u>. 1980; Barica 1989) due to a number of factors, algal uptake can be dismissed as the primary cause of this depletion. Loss of un-ionized ammonia to the atmosphere at elevated pH levels and water temperatures appears to be a possible explanation. A similar event was described earlier by Stratton (1969), Weiler (1979), and Murphy and Brownlee (1981) for eutrophic impoundments and lakes, which were able to liberate significant quantities of gaseous ammonia nitrogen to the atmosphere due to natural degasification processes, especially during windy days. Measurement of ammonia volatilization was not an objective of this study; however, differences between concentrations at the surface and deeper layers provide some basis for making crude estimates.

This can be achieved by estimating rate constants of toxic ammonia at the surface for the periods when NH_3 -N levels were dropping. This approach is presented in Table 1 for 1 - 3 week intervals of the summer season, when toxic NH_3 -forming conditions prevail due to high water temperatures and ammonia declines substantially. Site No. 3 (the ship canal) was disregarded. Most of the resulting daily rates for toxic ammonia loss from the top layer were between 22=56 µg/L/day toxic NH_3 -N; in average 35 µg/L/day or, 3.5 mg/m²/day,

-17-

i.e. 3500 g/km^2/day or 75.25 kg/lake/day. Using a conservative estimate for the length of favourable conditions for volatilization (three summer months or 90 days), this corresponds to 6.77 tons of ammonia per summer season.

It can be assumed that the loss of ammonia is possible as long as un-ionized toxic species is present and there is sufficient wind action to enable the transfer from water surface to the atmosphere. The estimate of ammonia lost through volatilization, although important in reducing acute toxicity to fish, represents less than one day's loading of ammonia from both municipal STPs (7.5 tons/day; DOE-MOE 1989) during the summer months and is insignificant in the overall ammonia budget of Hamilton Harbour.

Figures 5-6 provide additional evidence of ammonia volatilization. While dependence of toxic ammonia on water temperature is linear and significant at the depth of 5 m (Fig. 5), it is insignificant at the surface, suggesting that meteorological conditions (wind velocity, barometric pressure, wave action, etc.) govern the removal of accumulated un-ionized ammonia gas from the lake surface. Combined plots of all sites (Fig. 6) for toxic ammonia versus pH, water temperature and total ammonia indicate a poor curvi- linear correlation, suggesting that other factors are active players, as mentioned earlier.

Spatial distribution of ammonia species

Figure 7 presents areal distribution of the total and un-ionized toxic ammonia for 4 characteristic periods, beginning with total depletion (fall) and maximum toxic levels (summer). (For a full account of 15 areal distribution maps, see Barica and Vieira 1988.)

-18-

zonation and seasonality: Ammonia concentrations are not evenly Areal distributed over the whole area of the harbour and show a distinct areal There are two main distribution zones in the Harbour: the zone zonation. east of the deepest spot, (Site 5) which is affected primarily by Hamilton STP industrial effluents and to a large extent by the Burlington STP outfall, outfall (Site 6). This zone is affected at the same time also by the water exchange with Lake Ontario. Depending on the thermal and flow conditions in the ship canal, it shows either a dilution effect or a short-circuited flow the south-east arm directly into Lake Ontario, without adequate mixing from the rest of the Harbour (Barica et al. 1988). Another zone, the western with of Hamilton Harbour, is significantly less affected by STP discharges half from both sources.

The concentrations of total NH_3-N at all sampling sites were highest in the spring and gradually decreased to their minimum in the fall (October) This agrees with the seasonal distribution graphs shown in Figures 2-3.

<u>Patchiness of toxic ammonia</u>: Toxic ammonia levels do not show any correlation with total ammonia levels. They usually exceed the IJC objective of 20 μ g/L over the entire Harbour for most of the year, but are highest in the summer, when the total ammonia levels are lowest. Also, toxic ammonia levels are often lower in the most ammonia-polluted southeast arm than in the rest of the harbour. There are occasional isolated spots of toxic ammonia levels exceeding LC₅₀ which are presumably caused by localized warm water slugs from unidentified sources. This suggests that the fish populations are not exposed to sublethal or toxic levels over the entire area of the harbour and can obviously find a refuge in the safe parts of the lake. Patchiness ammonia distribution in Hamilton Harbour explain why the warm-water fish populations are able to survive these conditions despite the toxic pressure.

Impact of Western Lake Ontario

On a number of areal distribution maps, (Fig. 6, and Barica and Vieira 1988) the ammonia plume from Hamilton Harbour can be followed into Lake Ontario. This was particularly noticeable on May 5, 1988 and agrees with the previous conclusions (MOE 1986). The elevated ammonia levels, however, disappear quickly through dilution, algal uptake and nitrification and the effect does not exceed an area of 2-3 km radius from the ship canal. The effect of Hamilton Harbour on the quality of Lake Ontario can therefore be considered minimal (Barica <u>et al.</u> 1988).

Pathways of ammonia in Hamilton Harbour

Figure 8 presents the distinct pathways of nitrogen compounds moving through the Hamilton Harbour in two directions: : 1) from the Hamilton STP outfall eastward to the Ship Canal (Sites 1,2 and 3) and, 2) from the Burlington STP westward (Sites 6,5 and 4), in discrete sampling layers (1, 5 and 10 m). Total dissolved N (TDN) shows the expected path, i.e. a gradual decline from the maximum at the main source (Hamilton STP) and the minimum near the Ship Canal (Site 3, with dilution effect of Lake Ontario water). The second path is from a lesser maximum near the outfall from the Burlington STP (Site 6) and remains almost constant across the lake.

Total and toxic NH_3-N follow almost identical lines suggesting that the TDN input consists mostly of ammonia, with some minor proportion of dissolved organic N. Surprisingly, the peak for toxic NH_3-N in the second path is highest at Site 5 rather than 6 where it originates. This can be explained by hydrological conditions, with site 5 being affected by both path 1 and 2 through a combined effect.

Site 3, as expected, shows the lowest levels of all parameters due to the diluting effect of Hamilton Harbour.

Nitrate and nitrite concentrations do not follow this pattern, and show more uniformity throughout both paths. Only the dilution effect near Site 5 is clearly noticeable. However, there are significant differences in the pH pathways: the first path shows the lowest pH values near the Hamilton STP (Sites 1,2) - presumably due to acidity of treated effluent. The second path shows the highest pH at Site 5, which appears to be affected by more alkaline discharges from the Burlington STP (Site 6).

Dissolved oxygen and chlorophyll a increase gradually from Sites 1-3 northward and then westward (Sites 6-5-4). The main body of Hamilton Harbour, not affected directly by either the Hamilton STP, or Ship Canal water exchange (Sites 4,5 and 6), or hydraulic short-circuiting behaves as a natural

-21-

productive lake. The south-eastern arm with the highest loading of nutrients is also the least productive, likely due to the adverse effects of pollution on chlorophyll a production.

DISCUSSION

Elevated ammonia levels originating from external or internal sources are a frequent phenomenon in fish ponds, hypereutrophic lakes, and polluted harbours. However, elevated levels do not usually develop toxic conditions. Hamilton Harbour's high ammonia levels are comparable perhaps to Lake Orta in Italy, polluted by ammonia effluents from a textile industry at low pH, but with no formation of toxic ammonia (Mosello <u>et al</u>. 1986).

Several studies on ammonia and nitrate cycling in Hamilton Harbour have been previously conducted (Harris <u>et al</u>. 1979 a,b, 1980; Morgan 1979; MOE 1981, 1985), which agree with our results to a large extent as far as the seasonal cycles are concerned. However, little or no attention has been paid to ammonia dissociation into the toxic species. Likewise, areal zonation has not been considered and nitrite was not considered a significant contaminant (Harlow and Hodson, 1988). This study was designed to fill existing gaps and provide updated information on the recent state of ammonia and nitrite contamination, prior to introduction of remedial measures.

As the Remedial Action Plan (RAP) process has demonstrated (DOE-MOE 1989), ammonia loading and concentrations have been steadily decreasing since the early 80's due to improved wastewater treatment technologies. This study suggests that the nitrogen cycle in Hamilton Harbour is deformed by the excessive loadings of NH_3 which possibly inhibit the nitrification process, particularly formation of NO_3 . The intermediate process, i.e. the production of NO_2 -N, appears to be more responsive and less inhibited. While concentrations of ammonia vary between overload levels to values close to zero, the temporal variability of nitrate concentrations is less pronounced. Algal uptake and volatilization are assumed to be the major factors governing ammonia regime rather than nitrification, which does not appear to be stoichiometrically proportional to ammonia losses and may be inhibited by extremely high ammonia levels (Lewis <u>et al</u>. 1986).

The total ammonia cycle, while still to a large extent affected by the nitrification process, is perturbed by water exchange and short-circuiting of effluents. There is no toxic ammonia cycle in a true sense - it is governed entirely by elevated pH values and frequent intrusions of warm water slugs, presumably from the steel industry. The distribution of ammonia across the lake is also not homogeneous. Ammonia concentrations show rather a strong patchiness depending on the above mentioned factors.

Volatilization of ammonia from Hamilton Harbour's surface is obviously another reason for the absence of distinct cycles of toxic ammonia. Figs. 5 and 6 suggest that there is no significant correlation of toxic NH₃ either with total NH₃-N and water temperature, or even with pH at the surface of the lake, as expected from equation (1). The explanation is that toxic ammonia concentrations are controlled by factors other than pH and temperature particularly volatilization during periods of high wind and wave activity. Loss of gaseous ammonia species affects the overall concentrations of total ammonia and total dissolved nitrogen; hence the discrepancies with a "normal" nitrogen cycle in a "normal" lake.

-23-

Sites with the highest total NH_3 -N concentrations (1 and 2 downstream Hamilton STP and site 6 near Burlington STP outflow) do not show the highest toxic levels as expected. This is mainly due to lower pH values of treated STP effluents affecting these areas.

All discharges from STPs and industries around Hamilton Harbour meet existing standards for wastewater treatment (MOE 1986). Also, all effluents were deliberately discharged into Hamilton Harbour rather than Lake Ontario where the dilution effect would be less noticeable. This was done to take advantage of Hamilton Harbour as a "stabilization pond" to store the effluents before they are released into Lake Ontario (Forde 1979). While the presence of high concentrations of nitrogen (as nitrate) is beneficial to the eutrophic system to maintain high N:P ratios which favour development of green rather than obnoxious and scum-forming blue-green algae (Forsberg 1979), the ammonia levels must be further reduced to meet the IJC objective of not exceeding 20 $\mu g/L$ of toxic NH₃-N and avoiding periods with lethal concentrations. This is being realized by the RAP by proposing a nitrification stage for municipal wastewater treatment (DOE-MOE 1989).

Due to the irregularities of toxic ammonia incidents, their short duration and limited extent with distinct areal patchiness, the fish populations in the harbour are able to survive toxic episodes of both ammonia and nitrite by finding refuge in non-toxic areas. Acclimatization, predominance of coarser fish species and availability of large refuge areas in the Harbour are factors enabling survival of warm-water fish populations, which are less sensitive to ammonia than the cold water species (U.S. EPA 1985).

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-24-

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| STATION | | 1 | | 2 | 4 | | 5 | 6 | |
|---------------------------------|-----|------|------|----------|---------|--------------|----------|---------------|------|
| Date | 5.5 | 11.5 | 21.5 | 12.8 3.9 | 5.5 11 | .5 11.5 21.5 | 12.8 3.9 | 5.5 11.5 16.7 | 28.7 |
| Conc. at surf. (ug/L) | 583 | 245 | 68 | 503 54 | 316 | 183 591 59 | 141 17 | 315 112 277 | 122 |
| Diff. per interval (ug/L) | 338 | 171 | | 449 | 133 | 532 | 124 | 193 | 234 |
| Interval (days) | 6 | 10 | | 20 | 6 | 10 | 20 | 6 | 12 |
| Diff. per day | 56 | 17 | | 22 | 22 | 53 | 62 | 32 | 19 |
| Mean diff. | | | | - | 35 ug/l | L/day- | | | |

Tab. 1 Rate constants for the loss of unionized toxic ammonia through volatilization over specific time intervals of time during the summer of 1987 (ug/L).

Fig. 1 Location of sampling sites in Hamilton Harbour. @Vertical profiles. O surface sites.





Fig. 2 Seasonal distribution of ammonia and nitrite together with selected water quality parameters in Hamilton Harbour 1987-1988. Sampling sites 1,2 and 6; directly affected by effluents from sewage treatment plants in Hamilton and Burlington. 10 m average values.



Fig. 3 Seasonal distribution of ammonia and nitrite together with selected water quality parameters in Hamilton Harbour 1987-1988. Sampling sites 4,5 and 3; relatively unaffected by the effluents. 0-10 m average values.



Fig. 4 Characteristic vertical profiles of ammonia and nitrite together with selected water quality parameters in the deepest spot in Hamilton Harbour (24 m, Site 5) before and during the stratified period. More profiles available from Barica and Vieira 1988.



Fig. 5 Relationship of toxic ammonia to water temperature at two surface layers in Hamilton Harbour. A-insignificant, B-significant at 0.01 level.





TOXIC NH_3 -N, μ g/L Relationship of toxic ammonia to total ammonia, water temperature and pH. Surface, sites 1-6 all together. 1987-1988 data. Insignificant Fig. 6 linear correlations; poor curvi-linear correlations.



Fig. 7 Characteristic areal distribution of total and toxic un-ionized ammonia voer a nitrification cycle.



Fig. 8 Longitudinal pathways of ammonia, nitrite and other selected parameters from the treated municipal sewage discharges (Sites 1 and 6) across Hamilton Harbour.

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