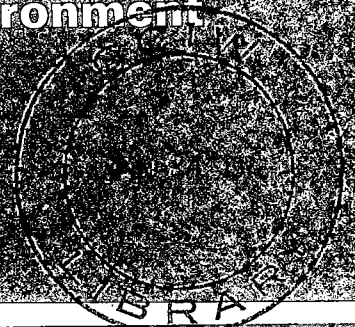


Nitrilotriacetic Acid (NTA) in the Canadian Environment

D. H. Matheson



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SCIENTIFIC SERIES NO. 74
(Résumé en français)

INLAND WATERS DIRECTORATE
WATER QUALITY BRANCH
OTTAWA, CANADA, 1977





Environment
Canada

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Abstract

Nitrilotriacetic acid (NTA) has been used in Canada since 1970 as a replacement for phosphate in detergents. An extensive monitoring program for NTA residuals in water supplies has been carried out by the Water Quality Branch, Inland Waters Directorate, Department of Fisheries and the Environment, with the close cooperation of the Procter & Gamble Company of Canada, Limited. The program includes a survey of public water supplies across Canada and intensive studies of 13 municipalities and certain unique local situations.

To date the findings of this program are:

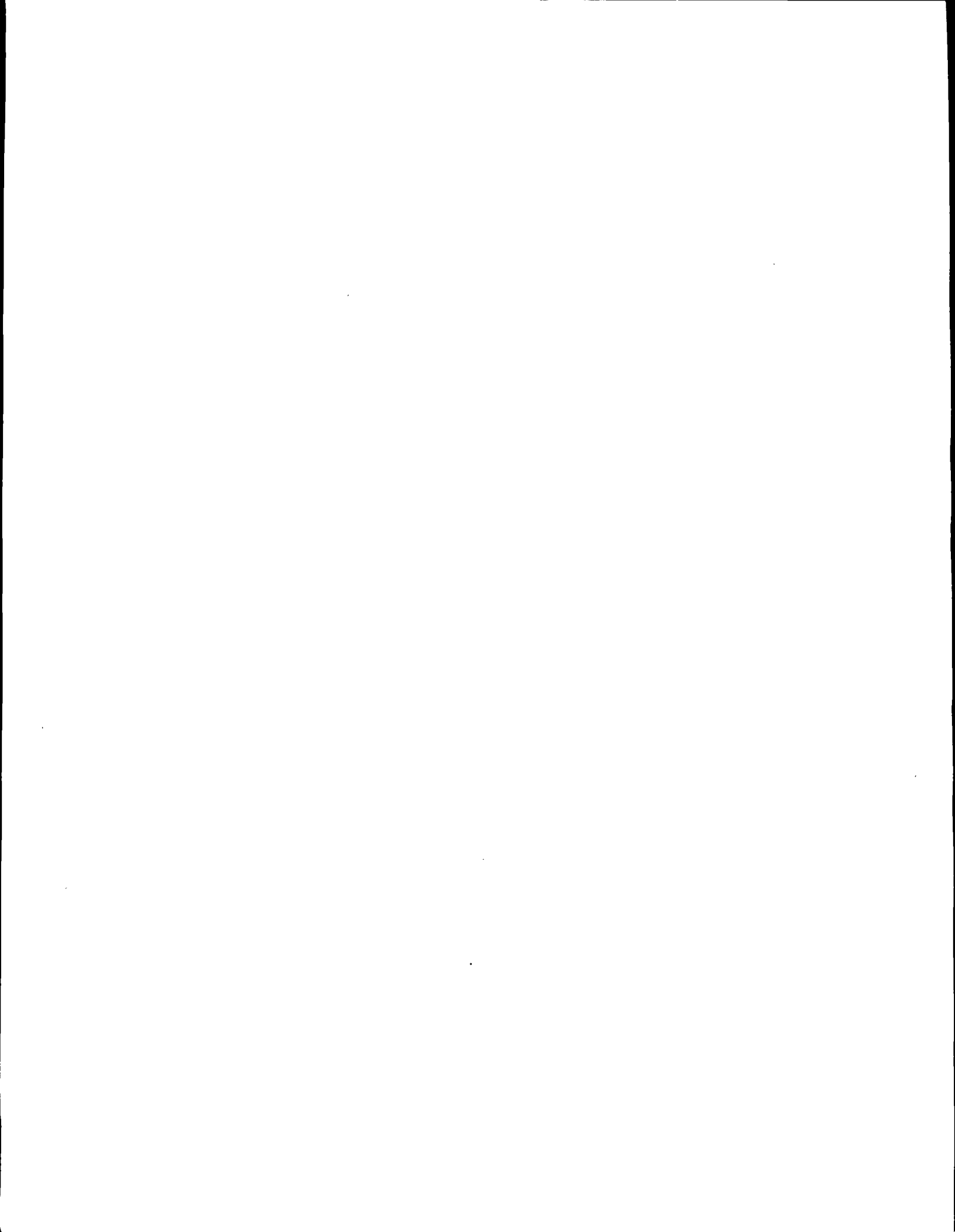
- 1) Rapid disappearance of NTA in wastewater treatment plants and in receiving waters has prevented a build-up of the concentration of the chemical in the environment despite its expanding use.
- 2) Very few cases occurred in which the NTA content of drinking water derived from surface sources exceeded 10 ppb. These happened where the raw water was polluted with wastewaters containing NTA and reused before degradation and dilution had reduced the concentration.
- 3) Shallow groundwaters may be contaminated by NTA by way of faulty septic tanks or disposal pits, but they should be condemned for more urgent sanitary reasons. Municipal groundwater supplies showed little evidence of NTA contamination.

Résumé

L'acide nitrilotriacétique (NTA) est utilisé au Canada depuis 1970 pour remplacer des phosphates dans les détergents. La Direction de la qualité des eaux de la Direction générale des eaux intérieures, ministère des Pêches et de l'Environnement, avec l'étroite collaboration de *Procter & Gamble Company of Canada, Limited*, a exécuté un important programme de surveillance des résidus de NTA dans les réserves d'eau. Le programme comprend notamment une étude des approvisionnements publics en eau à travers le Canada et des études intensives de 13 municipalités et de certaines conditions locales exceptionnelles.

À l'heure actuelle, ce programme a établi que:

- 1) La disparition rapide du NTA dans les usines de traitement des eaux usées et dans les eaux réceptrices a empêché l'accumulation de ce produit dans l'environnement malgré son usage croissant.
- 2) La teneur en NTA de l'eau potable provenant de sources superficielles a très rarement dépassé 10 ppb et seulement lorsque l'eau était polluée par des eaux usées contenant du NTA et réutilisée avant que la dégradation et la dilution n'en aient réduit la concentration.
- 3) Les eaux souterraines près de la surface du sol peuvent être contaminées par le NTA à cause des fosses septiques ou des puits de décharge défectueux, mais elles devraient être condamnées pour des motifs plus impérieux d'hygiène. Les sources municipales d'eau souterraine étaient très peu contaminées par le NTA.



Introduction

In 1964, the Governments of the United States and Canada, having reason to believe that the pollution of Lake Erie, Lake Ontario and the international section of the St. Lawrence River was substantial, asked the International Joint Commission to inquire into and report on the causes and extent of the pollution and to recommend remedial measures. In the resulting report published in 1969, the findings concluded that accelerated eutrophication, particularly of Lake Erie, was taking place and producing deleterious effects and that an important cause was the addition of excessive amounts of nutrient elements, especially phosphorus, to the lakes. A program for reducing the phosphate input to the lakes was suggested which recommended:

- a) the reduction of the phosphorus content of detergents and the amount of phosphate-based detergents used, and the complete replacement of phosphorus compounds in detergents by environmentally less harmful substitutes as soon as possible, but not later than 1972 and
- b) the incorporation of phosphate-removal processes in wastewater treatment plants.

In Canada, both of these proposals were acted upon. Serious questions, however, were raised concerning the possible environmental and public health effects that might be produced by the introduction of a new substance as a replacement for phosphate in detergents. Nitrilotriacetic acid (NTA) appeared to be the material most likely to be used. The quantities involved would be very large if complete replacement of phosphate could be achieved, and little was known about the persistence of the chemical in the environment and its possible effects. A Canadian national NTA monitoring program was therefore established in late 1971 to acquire data upon which appropriate conclusions could be based. In this report, findings of the program are discussed in some detail and conclusions and recommendations concerning NTA in the environment are given. For additional information, one may refer to *NTA (Nitrilotriacetic Acid) — An Ecological Appraisal*, which was prepared concurrently with this report and provides an overall view of the general and specific effects of NTA on the aquatic ecosystem and the biota. It was written by

Prakash (1976) for the Water Subcommittee of the National Research Council Associate Committee on Scientific Criteria for Environmental Quality.

In the United States, as well as in the Scandinavian countries, a considerable use of NTA as a detergent builder developed in the 1960's. In December 1970 in the United States, the Surgeon General asked for a discontinuance of its use for this purpose, as a result of the concern expressed for the possible health effects that might be produced. This restriction, which was voluntarily accepted by the American detergent industry, had the effect of preventing the growth of NTA usage; it is now employed on a relatively small scale for special industrial purposes. In Canada, on the contrary, the restrictions on the use of phosphate builders resulted in a rapid increase in NTA consumption.

On August 1, 1970, regulations were put into effect in Canada limiting the P_2O_5 content of detergent products to 20%. In May 1972, a ministerial announcement was made that the allowable P_2O_5 content would be further reduced to 5%, effective January 1973.

With the eventual widespread restriction on phosphate use in view, the detergent industry increased its efforts to find and develop suitable replacement materials. By the early 1960's, NTA had become commercially available at acceptable costs and was the chief contender based on its performance characteristics and because serious environmental effects were not expected.

Therefore in Canada, as phosphates were restricted, the use of NTA increased steadily. In the early part of 1972, the industry-wide average NTA content in detergents was 6%. In 1973, the 250 million pounds of detergent products purchased and used in Canada had an average content of 15% NTA. This resulted in the discharge of 37.5 million pounds of NTA to the environment by way of wastewater. Viewing this in a proper perspective as significant point sources, a city with a population of one million would have discharged 5,000 pounds of NTA per day, with an average concentration in its wastewater in the order of 5 ppm.

The program for monitoring NTA in the Canadian environment, commenced in 1971, has been carried out by the Inland Waters Directorate, Fisheries and Environment Canada, with the close cooperation of the Procter & Gamble Company of Canada, Limited.

The program has included:

- a) A survey of the NTA content in the finished drinking water in municipalities across Canada. Four annual samplings have been made to date.
- b) Sampling of raw waters above and below 13 selected municipalities and the municipal tap water. Monthly samples have been collected since 1971 and analyzed by Procter & Gamble.

c) The St. Lawrence River Water Quality Surveillance Study of 1974, which involved NTA determinations on samples collected from the international section of the river.

d) The study of some unique situations in detail: Hamilton Harbour, the western end of Lake Ontario, rivers in the metropolitan Montreal area, and several selected groundwater situations. These are discussed later.

Two analytical methods were employed by both laboratories concerned. The interlaboratory comparisons are discussed, and some problems encountered in the interpretation of the data are considered at length.

The National NTA Monitoring Program

INTRODUCTION

Background

Because of the evident need to reduce the input of phosphorus to surface waters and the resultant restrictions on the use of phosphates as builders in detergent formulations, the detergent industry turned its attention to identifying and developing suitable substitutes. Among the relatively few possibilities, NTA was considered the best substance.

The function of the builder in the detergent product is to eliminate the effects of calcium and magnesium cations on the performance of the detergent. This can be accomplished in two ways: by precipitating these cations as insoluble compounds or by sequestering them in the form of water soluble complexes. When precipitation reactions are used the insoluble precipitates must be kept in suspension in the wash water to avoid redeposition of the curd-like precipitate and the removed soil on the goods being washed. When sequestering agents are used the cations are kept in solution, the objectionable precipitates are not formed and the removed soil is easily rinsed away.

To be acceptable as a substitute builder, a substance should be safe for use in the household situation. The formulations should have an adequate performance and thus be accepted commercially, and no undesirable effects should be produced in the environment when the substances are used in the large quantities associated with the present scale of detergent use.

Among the possible inorganic materials that might replace phosphate are sodium carbonate, borate or silicate. All of these produce a high pH and precipitate hardness. Organic compounds, including citrate, NTA and ethylenediamine tetraacetic acid (EDTA), are sequestering agents. Citrate quite evidently would be innocuous in the environment since it readily and quickly degrades, but its sequestering powers are inadequate. EDTA sequesters powerfully, but is not considered to be suitable for use in general purpose detergents because of its cost and its low biodegradability.

NTA was the builder of choice since it is effective in its performance, safe in home use in the formulations marketed, and it appears to be relatively innocuous in its environmental effects.

Early Concerns

When the possible large-scale use of NTA was first being considered, the areas of concern were:

- a) whether NTA would degrade or accumulate in wastewater treatment and/or in the environment;
- b) if it did accumulate because of slow degradation what concentrations could be expected; and
- c) the effects of the resultant concentrations with respect to i) toxicity to the biota, from NTA itself, from its degradation products or as a result of extracting trace metals from natural sediments or industrial waste deposits; ii) enhancement of the eutrophication of waters by the added nitrogen; and iii) toxicity to man in the concentrations in which it would occur in drinking water, as NTA or metal complexes.

A large amount of work has now been completed and the answers to most of these questions are well known. They are discussed in detail in the following sections.

Biodegradation

The biodegradation of NTA under aerobic conditions in a natural situation and in biological wastewater treatment plants is well established. The naturally occurring bacterial flora become acclimatized after a period of exposure to NTA and then degrade the compound rapidly. The acquired ability to degrade NTA is retained for some time if the substance is temporarily absent. Mutant strains have been developed which are capable of utilizing the material without acclimatization, and the rate of consumption expressed in weight of NTA used per unit of cell mass is very high.

The performance of various types of aerobic wastewater treatment processes has been observed. The efficiency of removal is highly temperature-dependent, varying from 95% at 20°C to 50% at 5°C in well-run activated sludge plants. Lagoons in cold climates operate at lower temperatures than activated sludge plants and consequently exhibit poorer removals in winter. Un-aerated lagoons may freeze over and become anaerobic, and under these conditions the removal of NTA is nearly zero.

There are few data available on the operating performance of actual plants, especially the larger plants. Rudd, Townsend and Hamilton (1) have published a limited amount of data on effluent concentrations from the Winnipeg activated sludge plant. Figure 1 shows their data. The effluent concentration increased steadily from the end of 1971, the maximum being observed in August 1972. No data were available for influent concentrations, but this was in a period of increasing NTA usage.

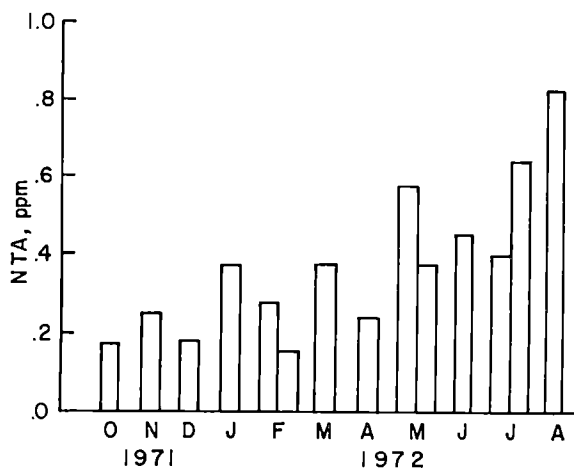


Figure 1. NTA in effluent, Winnipeg sewage treatment plant.

Good information on the NTA removal performance of large wastewater treatment plants is especially important, as by far the largest percentage of the NTA output to the environment occurs at point sources in these effluents. Unfortunately there is only a small amount of these data published. Casual sampling does not provide very useful information because of the wide range of the diurnal variation of NTA in the influent; the residence time of the water in the plant; and the many plant operating variables (contact times, mixing, mixed liquor suspended solids) which affect the removal efficiency. Flow-weighted composite sampling of inflow and outflow over some period of time is necessary as the minimum requirement. It has also

been shown in experimental plants with a constant input of NTA that fluctuations in removal efficiency occur which are attributed to changing populations of organisms in the activated sludge. The winter performance of large treatment plants may be better than would be anticipated from studies on small plants, since the temperature in large aeration tanks does not fall as low.

Laboratory and pilot plant experiments indicate that after acclimatization, degradation in aerobic treatment is rapid and complete; the end products are CO₂, NH₃ or NO₃ and H₂O. The intermediate metabolic products of bacterial degradation were not found.

Wastewater treatment systems operating under near anaerobic conditions (septic tanks, facultative lagoons and ice-covered lagoons) show little, if any, reduction in NTA during passage through the plant. Septic tank effluents discharged into well-aerated drainage fields, however, are effectively stripped of NTA by the action of acclimatized soil bacteria.

NTA can gain access to aquifers and especially to shallow aquifers by the downward movement of water from water-logged septic tank drainage areas or leakage from the anaerobic sections of lagoons. In anaerobic groundwaters, slow degradation of NTA by the indigenous bacteria takes place with the production of methane and carbon dioxide. The extent of this cannot be estimated properly at the present time, since little is known about the microbiological activity in aquifers.

The use of anaerobic sludge digestion (which is commonly a part of modern wastewater treatment) is of little consequence in the survival of NTA. It has been shown that neither NTA nor its metal chelates adsorb on primary or activated sludge (2, 3), and consequently do not enter the anaerobic digestion stage in appreciable quantities. In any case, the supernatant from the digesters is recycled through the aerobic stages.

Transport of Heavy Metals

The effect of undegraded NTA carrying chelated heavy metals through a wastewater treatment plant to the receiving water is not significant. At Waterdown and Gloucester, Ontario, work on small activated sludge plants treating purely domestic sewage containing natural amounts

of metals showed no significant transport of metals. In situations where abnormally high levels of metals are present (for example, because of the inclusion of industrial wastes in the wastewater) the passage of some metals with undegraded NTA may occur. The metal ions in the NTA-metal chelates disappear rapidly from solution once the NTA molecule has been degraded in the receiving water (4).

Similarly, a substantial uptake by residual NTA of heavy metals in lake or river sediments is very unlikely. In the first place, the NTA in wastewater effluents is already chelated with the metals originally present in the wastewater and secondly, natural contact of the NTA with deposited sediments is minimal. Experiments involving the stirring of sediments with water containing NTA (thus providing unrealistically high contact opportunities) show that uptake does occur, but the existence of soluble metal compounds is transitory as dissociation of the complexes and degradation of NTA take place (4). In a situation that is highly significant with respect to public health, NTA has not been found to mobilize mercury present in abnormally high levels in the muds of Lake St. Clair (5).

Degradation in Receiving Waters

Biodegradation continues in waters receiving wastewater effluents, but its assessment is difficult for several reasons, including the lack of information on the processes involved. An allowance must be made for the initial effects of the dilution ratio in streams and diffusion in larger water bodies. If these can be known well enough the calculated concentrations can be compared with measured values. The difficulties here are those associated with getting truly representative samples. In streams, the influent wastewater stream may travel along the riverbank for long distances without mixing with the main flow. In large quiescent water bodies, the dilution and diffusion of the wastewater inflow depend on thermal stratification and the existence of bistable coastal jet currents, which move the partly diluted wastewater up and down the coast while at the same time holding it near the shore.

Laboratory studies have shown that chelates of NTA with certain metals are resistant to biodegradation (4), and it may be that at least part of the NTA escaping from treatment plants is in the resistant chelate form. NTA in this combination would be expected to survive longer in the receiving waters than free NTA or NTA combined in easily dissociated chelates. The reported values of the half-life of NTA in receiving waters vary from minutes to months and are no doubt affected by the chelated form, the presence of other heavy metals, and the concentration and biological capabilities of the bacterial population.

Photochemical decomposition of NTA in open surface waters may well be an important process. This may be comparable in magnitude with biological degradation, especially in clear waters with large exposed surface areas. An estimation of the rate of photochemical decomposition of NTA in very clear waters indicates a half-life of about two months (Dr. J. Carey, personal communication) (Appendix D).

Since NTA is substantially degraded in in-plant and after-treatment processes, it is apparent that NTA will not accumulate in natural waters to a significant extent. Locally it will be present in receiving waters in close proximity to treated wastewater discharges, and it will be present in drinking water in situations where the water must be reused for public water supplies with only brief storage. In contrast with wastewater treatment, the usual processes of water purification do not remove NTA biologically. Activated carbon which is employed in some water purification plants to remove organic matter (particularly taste- and odour-producing substances) may remove NTA also. This appears not to have been investigated, but if it is effective it would provide an additional argument for the use of carbon to reduce the concentration of all kinds of unidentified organic matter having unknown effects. The effect of chlorination on NTA at the levels employed in water purification is not well documented. It is likely that where free residual chlorination is practised and detention with a high residual for several hours occurs, some substantial proportion of the existing NTA will be destroyed.

Health Effects

While a review of the health aspects of NTA is not a part of the present study, it is important to be aware of the developments in the field.

Although there has been an increase in NTA utilization, there has not been any build-up in concentrations in potable or raw water supplies. This is confirmed by the monitoring program described in this report. The levels now found in Canada in public water supplies are very low, usually less than 10 $\mu\text{g/l}$. One community (Brantford, Ontario) has levels usually between 15 $\mu\text{g NTA/l}$ and 30 $\mu\text{g NTA/l}$; one sample has contained 50 $\mu\text{g NTA/l}$.

In studies of rats, the Health Protection Branch, Health and Welfare Canada (6), has failed to show any significant *in vivo* mutagenic potential for NTA at very high dose levels. These results agree with many studies on the mutagenic activity of NTA carried out by several other

laboratories. Cancer studies in the United States have shown that rodents fed extremely high levels of NTA have shown a carcinogenic response. During a life-time study no histological or biochemical changes could be detected in rats fed many times the possible intake by Canadians. A factor in excess of 100,000 exists between the levels usually found in drinking water in Canada and the "no-effect" level determined in laboratory animals. Health and Welfare Canada has thus concluded that no significant hazard to human health exists from the present usage of NTA.

Environmental Biological Effects

NTA introduced into the environment may have two possible effects: accelerating eutrophication through the additional input of nutrient nitrogen and exerting deleterious effects on the biota.

The use of NTA, whether it reaches the environment in undegraded or fully degraded form, represents a small increase in nitrogen input to the receiving waters. The quantity involved, however, is very small in relation to the normal constituent of sewage [probably less than 4% (7)] and can have only a negligible effect on normal inland waters in which nitrogen is not the limiting factor. In marine situations where nitrogen frequently is limiting, this small increment may be marginally significant.

The effect of added NTA on aquatic life also appears to be minimal. NTA is not toxic to organisms at a concentration two orders of magnitude greater than has been shown to exist in actual practice (8). Recent work in the United States indicates that at a maintained concentration of 0.2 mg/l, no alterations in algal species composition or in primary productivity can be detected and the utilization of other dissolved organic matter by heterotrophs is not impaired (9).

THE MONITORING PROGRAM

Sampling and Analyses

The national NTA monitoring program incorporates two routine sampling programs: a) a broad nation-wide sampling of treated municipal water supplies represented to date by four annual samplings and b) a more intensive study of 13 Ontario municipalities from which monthly samples of tap water and untreated river water above and below the sewer outfalls are analyzed. The first program is handled by Canada Centre for Inland Waters (CCIW); the second was undertaken by the Procter & Gamble Company in cooperation with the Ontario Ministry of the Environment and CCIW, and later became a part of the national monitoring program.

The non-routine sampling programs that are discussed here as "special studies" involved sampling at intervals over shorter periods than those covered by the monitoring programs.

Two methods of analysis are employed. CCIW uses the polarographic method developed by Afghan (10, 11). The minimum detectable concentration is 10 ppb, and concentrations are reported as less than 10 ppb, 10 ppb and above this, even multiples of 10 ppb. The Procter & Gamble samples are analyzed by the Environmental Trace Substances Research Center at the University of Missouri, using the gas chromatographic method of Warren and Malec (12). In both laboratories, the samples are preserved with formaldehyde, which is said to ensure stability of the contained NTA. The Procter & Gamble data are reported as Na_3NTA ; in this discussion, unless otherwise indicated, these values have been recalculated to H_3NTA for comparison with CCIW data.¹

Interlaboratory Comparison

To relate the data from the two laboratories an exchange of samples was arranged. These samples were routine samples of groundwaters, finished municipal tap waters, river waters and samples from Hamilton Harbour. For comparison purposes, 130 sets of data were available.

In the low parts per billion range it is necessary to compare data reported by Procter & Gamble in whole parts per billion numbers with the reports of less than 10 ppb from CCIW. Therefore the data are divided into two groups representing data above and below the 10-ppb level. Group 1 is composed of samples for which *either* laboratory reported values less than 10 ppb and Group 2 contains samples for which *both* laboratories reported values of 10 ppb or more.

Group 1 Samples

There were 64 sample sets in this group, and of these, 42 (66%) were reported as less than 10 ppb by both laboratories. Of the remainder, for 13 samples Procter & Gamble reported values higher than 10 ppb, while CCIW reported less than 10 ppb. There were nine samples for which CCIW reported values of 10 ppb or more, whereas Procter & Gamble reported numbers less than 10 ppb. These discrepant samples appeared to be randomly distributed among the sources. Considering that the values being measured are near the detection limit and that

¹ $\text{H}_3\text{NTA} \rightarrow \text{Na}_3\text{NTA}$ using a factor of 1.3455
 $\text{Na}_3\text{NTA} \rightarrow \text{H}_3\text{NTA}$ using a factor of 0.7432

variable delays occur in the time between the collection and analysis of the samples, a reasonably good agreement between the laboratories is shown.

There are, however, four samples in which a wide discrepancy exists, where values found by one laboratory were from 60 ppb to 130 ppb higher than those of the other. One pair, having consecutive laboratory numbers, might represent an accidental mix-up of samples, but the other two were unrelated samples analyzed at different times.

Group 2 Samples

The 59 samples in this comparison were subjected to a number of statistical analyses in an attempt to determine the relationships between the two sets of data. These analyses follow:

- a) Paired t-test to compare the average difference between the two laboratories (the data were first log-transformed to obtain an approximately normal distribution). The t-statistic was significant at the 0.05 probability level, indicating that the Procter & Gamble readings were higher (on the average) than the CCIW values.
- b) Two nonparametric analyses on the raw data (thus removing the requirement to impose any distributional assumptions on the data); these were the sign test and the Wilcoxon signed rank test. Both tests indicate that the Procter & Gamble readings were higher (on the average) than the CCIW values.
- c) Correlation analyses. The Pearson product-moment correlation coefficient was computed on the log-transformed data, yielding a statistically significant correlation coefficient ($r = 0.697$). A 95% confidence interval for the true correlation is (0.531, 0.811). A nonparametric correlation coefficient, computed on the ranks of original data (Spearman rank correlation coefficient), yielded a value of 0.698.
- d) Regression analysis. Linear regression analyses were performed on the data (logs) and the confidence limits were calculated. The linear relationships between the Procter & Gamble data and the CCIW data (both with CCIW data as the dependent and Procter & Gamble data as the independent) were highly acceptable. It is thus possible to predict CCIW values (or averages) from Procter & Gamble data and vice versa.

As a result of these statistical analyses, it is apparent that the Procter & Gamble values are significantly higher, on the average, than the corresponding CCIW values. Even though there is this difference in the absolute values, however, the significant correlation between the two methods (as indicated by the regression analyses) allows results from the two methods to lead to similar conclusions overall.

In view of the ranges actually seen in the environment, these analytical differences will not affect the interpretation of the data.

The possible causes of the discordant results might be that:

- a) Accidental contamination occurred during sampling or subsequent sample handling. This is strongly suggested by the erratic nature of the discrepancies.
- b) The two analytical methods may not measure precisely the same chemical entity. In most samples this may have only a minor effect. Interfering substances, however, might occur variably in the samples and be seen as NTA by one method and not by the other.
- c) The assumption of stability of the low levels of NTA in the samples during storage. Since the interval between sampling and analysis is variable and sometimes quite long, the possibility of changes owing to biological, chemical and photochemical reaction should be considered.

Interpretation of Monitoring Data

The variability found in the comparison samples clouds the interpretation of the monitoring data, which are based on spot samples taken at considerable intervals. A single sample taken from a highly variable source (such as a small river) has little meaning in itself, and when this uncertainty is coupled with the observed interlaboratory variations, the confidence limits which must be associated with each datum point become very large. It is impossible to calculate what these limits are, but the suggested range, from -50% to +100% of the indicated value, is not unreasonable. This wide range has not been considered explicitly in the interpretation of data elsewhere in this report, so it must be borne in mind that the scale on which NTA is measured is really much coarser than even that implied in the CCIW data reporting where values of less than 10 ppb, 10 ppb, and 20 ppb only are given.

Recommendations to Improve Data

To clarify this situation the following procedures are suggested:

- a) A study should be made of the stability with time of low levels of NTA in distilled water and in natural samples, using the present methods of sample preservation and exposing the samples to variation in environmental conditions (temperature, light) representative of those involved in shipping and storage before analyses.

- b) It should be determined whether biological, chemical or photochemical changes can take place in stored samples that would affect one analytical method more than another.
- c) Since one grab sample cannot be significant in representing a variable system, three or more samples should be taken at intervals at each station, analyzed separately and interpreted statistically. It is noted that in part of the St. Lawrence study, repeated samples were taken on some occasions. In general, these were not too informative, since in that particular area all samples were consistently below detection levels. In areas where measurable concentrations occur, repeated sampling would be invaluable in providing more significant data.

It is recognized that this modification would increase the cost of monitoring programs, but the extra cost might be offset by the much greater significance of the data. (As an example, consider five annual samples from one source: <10 ppb, <10 ppb, <10 ppb, 50 ppb, <10 ppb. The 50-ppb value may be valid, or it may be the result of interferences or errors in sampling or analysis.) If the annual sampling was made up of three samples taken at intervals of one hour or one day, the significance of what appears to be an aberrant reading could be seen.

NATIONAL MONITORING PROGRAM DATA

Summary of National Data

The monitoring program to date includes four annual samplings, beginning in December 1972. Table 1 sum-

marizes the data, showing the number of samples examined and the number of samples in which NTA was present at or above the detection limit of 10 ppb. Most of the samples were collected in cold months (December to April) when biological degradation in the wastewater treatment plants and in the receiving waters would be at a minimum.

The numbers of positive samples found each year from 1972 to 1974 appear to be doubling annually, but this must not be interpreted as indicative of a trend. The large number of positive samples in 1974 is accounted for by samples from the Montreal area only. This is a local situation and does not indicate a country-wide increase. Most of the positive samples do occur in Quebec, however, and this may be associated with the paucity of secondary sewage treatment plants in the Province.

Summary of National Data by Province

British Columbia

More than half of the 126 samples examined were taken from supplies derived from lakes, rivers and groundwater in 1973 (Table 2). No samples were collected from 1972 to 1974 in which NTA was present at detectable levels. In 1975, one sample from the district municipality of Campbell (Campbell River) contained 60 ppb, a value which is questionable until it is confirmed.

Alberta

Twenty-six samples were taken in the seven largest cities; the supplies were all derived from river sources (Table 3). The only positive values obtained were in the Medicine Hat samples of 1973 and 1974, which contained 10 ppb and 20 ppb, respectively. The source of the raw water here is the South Saskatchewan River.

Table 1. National Monitoring Program Samples

Province	Number of samples examined				Number of NTA positive samples			
	1972	1973	1974	1975	1972	1973	1974	1975
British Columbia	3	78	9	36	0	0	0	1
Alberta	6	7	6	7	0	1	1	0
Saskatchewan	6	8	5	7	0	2	0	2
Manitoba	6	8	7	7	0	1	0	0
Ontario	76	76	73	60	3	1	3	4
Quebec	60	58	54	57	0	2	11	16
New Brunswick	5	10	0	5	0	0	0	0
Nova Scotia	6	15	0	9	0	0	0	0
Newfoundland	0	4	5	0	0	0	0	0
	168	264	159	188	3	7	15	23

Table 2. Summary of British Columbia Samples

Source	Number of samples examined				Number of NTA positive samples			
	1972	1973	1974	1975	1972	1973	1974	1975
Lakes	0	11	1	7	0	0	0	0
Rivers	3	56	7	25	0	0	0	1
Ground	0	11	1	4	0	0	0	0
	<u>3</u>	<u>78</u>	<u>9</u>	<u>36</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>1</u>

Table 3. Summary of Alberta Samples

Source	Number of samples examined				Number of NTA positive samples			
	1972	1973	1974	1975	1972	1973	1974	1975
Rivers	6	7	6	7	0	1	1	0

Table 4. Summary of Saskatchewan Samples

Source	Number of samples examined				Number of NTA positive samples			
	1972	1973	1974	1975	1972	1973	1974	1975
Lakes	1	3	1	1	0	0	0	0
Rivers	4	4	4	5	0	2	0	2
Ground	<u>1</u>	<u>1</u>	<u>0</u>	<u>1</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>
	6	8	5	7	0	2	0	2

Table 5. Summary of Manitoba Samples

Source	Number of samples examined				Number of NTA positive samples			
	1972	1973	1974	1975	1972	1973	1974	1975
Lakes	3	4	4	4	0	0	0	0
Rivers	3	4	3	3	0	1	0	0
	<u>6</u>	<u>8</u>	<u>7</u>	<u>7</u>	<u>0</u>	<u>1</u>	<u>0</u>	<u>0</u>

Table 6. Summary of Ontario Samples

Great Lakes system	Number of samples examined				Number of NTA positive samples			
	1972	1973	1974	1975	1972	1973	1974	1975
Lake Superior to Detroit River	7	7	7	6	1	0	0	0
Lake Erie	4	4	6	4	0	0	0	0
Welland Canal	6	6	6	5	0	0	1	0
Niagara River	2	2	2	2	0	0	0	0
Lake Ontario	21	23	22	13	0	0	1	2
St. Lawrence River	2	2	2	2	0	0	0	0
Ottawa River	6	5	3	3	0	0	0	0
Small lakes	7	5	5	5	0	0	0	0
Small rivers	8	8	8	8	2	1	1	1
Groundwaters	13	14	12	12	0	0	0	1
	76	76	73	60	3	1	3	4

Saskatchewan

Twenty-six samples were taken in the six largest cities. Two positive values were found in the 1973 samples from North Battleford and Prince Albert, which contained 20 ppb and 10 ppb, respectively (Table 4). Both supplies are derived from the North Saskatchewan River. In 1975, two samples from North Battleford contained 10 ppb and 20 ppb.

Manitoba

The samples came from the four largest cities; one half of the total came from Winnipeg, which derives its water from Shoal Lake. Only one positive sample was found, and that was from Thompson (Burntwood River) and contained 20 ppb in 1973 (Table 5).

Ontario

The largest number of samples examined in the program was from Ontario (Table 6). The water supplies are derived largely from the Great Lakes and rivers system, but about one third of the samples came from supplies from sources including small lakes, small rivers and groundwater. In the 180 samples that were collected from the Great Lakes-St. Lawrence River and Ottawa River systems, five positive values were found, randomly distributed. The only significant concentration of positive samples occurred in the supplies taken from small rivers; of the 32 samples

examined, five were positive and four of these were from Brantford.

Brantford—The relatively few CCIW samples of Brantford tap water are supplemented by a much larger number of samples taken by Procter & Gamble (Table 7). The two samplings agree quite well on a point-by-point basis, bearing in mind that they were not taken at the same time nor from the same location.

Table 7. Comparison of CCIW and Procter & Gamble Data on Brantford Finished Water (ppb)

Year	Month	CCIW (as H ₃ NTA)	Procter & Gamble (as Na ₃ NTA)
1972	December	10, <10	9
1973	April	10	6
1974	January	30	6

The Procter & Gamble data, plotted in Figure 2, show a considerable month-to-month fluctuation. In this Figure, the concentration of NTA in the river water above the sewage outfall is also shown, as presumably it represents the raw water quality. It would be expected that the two would be approximately equal, since it is thought that normal water purification processes would not remove or destroy NTA. It is, however, evident that the concentration in the river water is much higher than it is in the finished water.

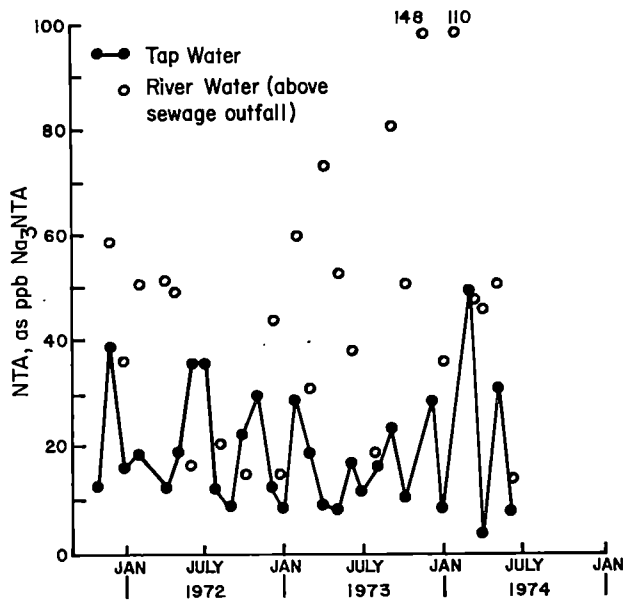


Figure 2. NTA in raw water and tap water at Brantford, Ontario (Procter & Gamble data).

The raw and finished waters are compared directly in Figure 3. Evidently there is a large scatter in the data which could exist because it is unlikely that the two samples represent exactly the same water mass. In Figure 3, the broken line passing through the origin has an equal number of points on each side and thus shows the correlation with as much significance as the data will allow. It appears from this that a reduction of NTA by about 50% occurs in the treatment, which could be interpreted as caused by a lack of an exact correspondence between the raw treated water samples or as evidence of an actual reduction during treatment. Treatment at Brantford includes prechlorination to yield a free chlorine residual of 3-4 ppm after one hour of contact; the application of powdered activated carbon for taste and odour control; coagulation with alum; and rapid sand filtration. Prechlorination and the activated carbon treatment have a potentiality to reduce NTA concentrations, the first by oxidation and the second by adsorption (18).

Chatham—The Procter & Gamble data are given in Figure 4. In the first half of the period of observation, raw water was taken from the Thames River. The river water averaged 24 ppb (Na_3NTA) in this period (15 samples), and the finished water, 15 ppb. In the other half where water was obtained by pipeline from Lake Erie, the finished water averaged 3 ppb Na_3NTA . This is in agreement with the 14 CCIW samples from municipalities using Lake Erie water which were all less than 10 ppb.

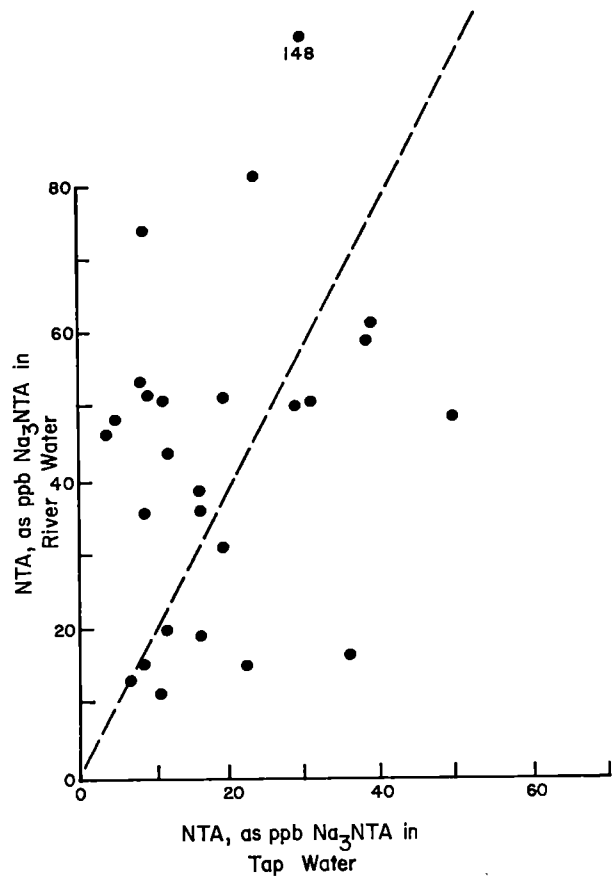


Figure 3. Comparison of raw water and tap water at Brantford, Ontario (Procter & Gamble data).

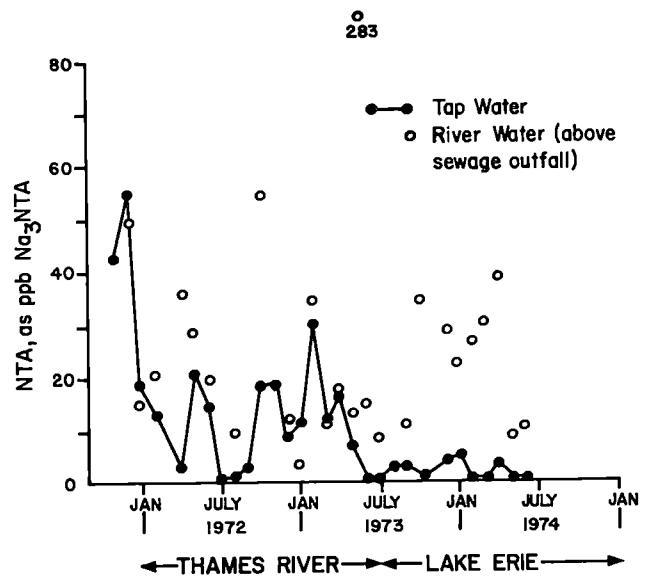


Figure 4. NTA in tap water at Chatham, Ontario (Procter & Gamble data).

Ottawa River—Twenty-three samples of finished water have been examined from five municipalities using Ottawa River water. These include Pembroke, Ottawa (two plants), Hull, Gatineau and Rockland. All of the samples contained less than 10 ppb Na₃NTA.

At Hawkesbury, Procter & Gamble has sampled river water above and below the sewer outfall and the finished water. Their data from December 1972 to June 1974 are summarized in Table 8.

The NTA in the river above the sewer outfall, presumably representing raw water, is compared with the finished water in Figure 5. There is a closer relationship between the two at Hawkesbury than is shown at Brantford, although there are three quite discordant values.

Because of the large dilution it is unlikely that the NTA inputs to the Ottawa River upstream from Ottawa could affect the water quality in the Ottawa area. The NTA input from a population of 500,000 in the Ottawa-Hull area, added to the mean flow of the river (32,000 cfs), would yield a concentration of 12 ppb (as H₃NTA), assuming no degradation in wastewater treatment or in the river. At Hawkesbury, sixty miles downstream, the measured concentration in the river is about 7-8 ppb H₃NTA. It is very

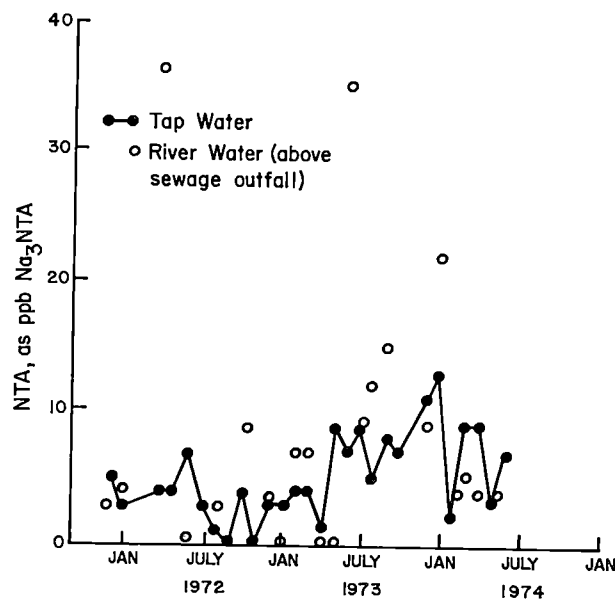


Figure 5. NTA in raw water and tap water at Hawkesbury, Ontario (Procter & Gamble data).

Table 8. NTA at Hawkesbury (ppb)

Source	Number of samples	Mean	Maximum	Minimum
River, above sewer outfall	20	10	35	0
Finished water	28	5.5	13	0
River, below sewer outfall	28	14	31	0

Table 9. Summary of Quebec Samples

Source	Number of samples examined				Number of NTA positive samples			
	1972	1973	1974	1975	1972	1973	1974	1975
St. Lawrence River*	4	4	4	4	0	0	0	0
Ottawa River*	2	2	2	2	0	0	0	0
Montreal area	15	14	13	13	0	1	8	6
Richelieu River	5	4	4	5	0	0	0	1
Yamaska River	3	3	3	3	0	1	2	2
Rivière l'Assomption	2	1	0	1	0	0	0	0
Small rivers	13	11	11	13	0	0	0	4
Small lakes	14	17	15	14	0	0	1	3
Groundwater	2	2	2	2	0	0	0	0
	60	58	54	57	0	2	11	16

*Excluding Montreal area

doubtful that such an amount of NTA could survive any wastewater treatment at the source plus degradation processes in the stream over a distance of sixty miles. It is concluded therefore that the observed concentrations at Hawkesbury represent local additions. The input from a population of 10,000 at Hawkesbury could not make more than an infinitesimal increase in concentration in the whole streamflow. The apparent increase of 4 ppb H₃NTA between points in the river above and below the sewer outfall cannot be considered significant.

Quebec

The Province of Quebec supplied the second largest number of samples and the largest number of positive samples. The distribution of sample points and the number of positive samples are summarized in Table 9.

Montreal Area—A large number of finished water samples have been examined from the Montreal metropolitan area, and many of these contained significant levels of NTA. The area is discussed in detail later; the conclusions are summarized here:

- a) There is substantially no NTA in the Ottawa and St. Lawrence river waters entering the area.
- b) The population in the area adds large amounts of NTA to the rivers in wastewater discharges. Mixing of the effluent streams with the river flows is not completed within short distances, and water containing NTA at levels higher than would exist if complete mixing had taken place is abstracted by downstream waterworks. The percentage of NTA in commercial products has increased since the beginning of the sampling in 1972, and the contributing population has also grown. It is therefore not surprising that an increasing percentage of water samples contain NTA at or above the detection levels.
- c) Downstream from the metropolitan area where mixing in the river is complete, the concentration of NTA in both finished waters and river water samples is below the detectable level.

The last finding is consistent with the calculated concentration of NTA in the river, derived from detergent use and the river flow. A population of 4×10^6 at Montreal, using detergents at the current rates, would add 2.6×10^6 kg H₃NTA to the river per year. The combined mean flow of the Ottawa and St. Lawrence rivers is 270,000 cfs. The resulting concentration of NTA in the river flow, without any allowance for degradation, would thus be only about 10 ppb.

Richelieu River—The Richelieu River is a stream of considerable size (mean flow 2,200 cfs) draining Lake Champlain and flowing straight north to discharge into the St. Lawrence River at Sorel, Quebec. The finished drinking water, sampled at five locations, has not shown a detectable level of NTA in the four annual samplings except for one value of 10 ppb at Sorel in March 1975 (Table 10).

Table 10. Richelieu River Samples (ppb)

Town	Samples examined			
	1972	1973	1974	1975
Saint-Jean	<10	<10	<10	<10
Chambly	<10	<10	<10	<10
Otterburn Park	<10	—	—	<10
Beloeil	<10	<10	<10	<10
Sorel	<10	<10	<10	10

Assuming a contributing population of 100,000, detergent usage at the 1974 rate, no degradation in treatment works or in the river, and a mean river flow of 2,000 cfs, the resulting concentration should be about 30 ppb. Since sampling indicates that the concentration is much lower than this, the reduction should be attributed to in-stream degradation.

Yamaska River—The Yamaska River is a small stream made up of several small branches. Cowansville on the Southeast Yamaska River has not shown detectable levels of NTA in the four annual samplings (Table 11). In contrast, Granby, a larger town on the North Yamaska River, has had positive findings in three of the four samples of the drinking water, the latest one containing 80 ppb. Saint-Hyacinthe, downstream on the main river, has shown the presence of 40 ppb in the 1974 and 1975 samples.

Table 11. Yamaska River Samples (ppb)

Town	Source	Samples examined			
		1972	1973	1974	1975
Granby	North Yamaska River	<10	20	20	80
Cowansville	Brome Pond on the Southeast Yamaska River	<10	<10	<10	<10
Saint-Hyacinthe	Yamaska River	<10	<10	40	40

Table 12. Small Lake Samples (ppb)

Town	Source	Samples examined			
		1972	1973	1974	1975
Alma	Lac-Saint-Jean	<10	<10	<10	<10
Baie-Comeau	Lac à la Chasse	<10	<10	<10	<10
Chibougamau	Lac Gilman	<10	<10	<10	<10
Drummondville	Lac-Saint-François	<10	<10	20	20
Grand-Mère	Lac-des-Piles	<10	<10	<10	<10
Hauterive	Lac Amédée	<10	<10	<10	<10
Kénogami	Lac Long	<10	<10	<10	<10
Mont-Laurier	Lac Thibault and Lac Roberge (formerly Lac à la Dam)	<10	—	—	<10
Noranda	Lac-Dufault	—	<10, <10 <10, <10	<10, <10	—
Rimouski	Lac à l'Anguille	<10	<10	<10	<10
Sept-Îles	Lac des Rapides	<10	<10	<10	<10
Shawinigan	Lac Lapêche	<10	<10	<10	20
Sherbrooke	Lac Memphrémagog	<10	<10	<10	10
Thetford Mines	Lac-à-la-Truite	<10	<10	<10	<10
Valleyfield	Lake St. Francis	<10	<10	<10	<10
Total samples		14	17	15	14

Table 13. Small River Samples (ppb)

Town	Source	Samples examined			
		1972	1973	1974	1975
Amos	Rivière Harricanaw	<10	<10	<10	<10
Asbestos	Rivière Nicolet	<10	<10	<10	<10
Charlesbourg	Rivière Montmorency	<10	<10	<10	30
Drummondville	Rivière-Saint-François	<10	<10	<10	20
Giffard	Rivière Montmorency	<10	<10	<10	<10
Joliette	Rivière l'Assomption	<10, <10	<10	—	<10
Jonquière	Rivière aux Sables	<10	<10	<10	<10
Matane	Rivière-Matane	<10	<10	<10	<10
Montmagny	Rivière des Perdrix	<10	—	<10	<10
Quebec City	Rivière Saint-Charles	<10	<10	<10	20
Rivière-du-Loup	Rivière-Verte	<10	<10	<10	<10
Saint-Jérôme	Rivière du Nord	<10	<10	<10	20
Victoriaville	Rivière-Bulstrode	<10	—	<10	<10
Total samples		14	11	12	13
NTA positive samples		0	0	0	4

Small Lake Sources—Fifteen municipalities taking water from small lakes were examined (Table 12). In 1972 and 1973, all of the samples contained less than the detectable level of NTA. In 1974, the sample from Drummondville contained 20 ppb, and in 1975, this sample and the two samples from Shawinigan and Sherbrooke were positive.

Small River Sources—Thirteen municipalities drawing water from small rivers were sampled (Table 13). All of the

samples were below the detection level in 1972, 1973 and 1974. In 1975, four samples from municipalities on four different streams contained 20 ppb and 30 ppb.

Groundwater Sources—Among the Quebec municipalities sampled, only two take water from groundwater sources. These are Saint-Raphaël (well) and Val-d'Or (springs). All samples in the four years have been below detection limits.

New Brunswick, Nova Scotia and Newfoundland

Fifty-nine samples were examined from the three provinces (Table 14). In all of the samples, NTA was reported as less than 10 ppb.

Table 14. New Brunswick, Nova Scotia and Newfoundland Samples

Province	1972	1973	1974	1975
New Brunswick	5	10	0	5
Nova Scotia	6	15	0	9
Newfoundland	0	4	5	0

NTA IN GROUNDWATER

General

Groundwaters are usually well protected against contamination from NTA. It has been well demonstrated (13) that NTA is rapidly removed from waters percolating through aerated soils after the bacterial flora have been acclimatized. When the soil is saturated and anaerobic conditions prevail, however, biodegradation is very slow, and undegraded NTA in wastewater can reach the groundwater.

The situations in which NTA may enter groundwater, discussed by Lawson (14), are:

- a) Seepage of polluted streamflow into the groundwater below the outfall of a sewage treatment plant. Since most treatment plants are located in areas where the flow is from the groundwater to the stream and a high dilution of the effluent takes place in the stream, this means of entry is of little importance. When effluents are discharged into small streams with little or no dilution water available, percolation to the water table is possible.
- b) Leakage through the bottom of sewage lagoons which are constructed on permeable soils. This leakage may create a dome of anaerobic water resting on the water table, feeding a constant stream of water containing NTA to the groundwater.

c) Faulty septic tank installation. Where a number of imperfect septic systems are located in villages and are of necessity in close proximity to wells, a sanitary problem results, which includes not only a concern for the effects of the NTA contamination but also an ever-present hazard of enteric disease transmission. Many such situations exist throughout the country in villages without proper water supplies or wastewater disposal systems. The inhabitants being made aware of the disease hazard can protect themselves by manual chlorination of the wells or by boiling drinking water, but there are no satisfactory home methods for removing NTA. Consequently, a small proportion of the population will be exposed to NTA intake via drinking water as long as NTA is used in detergents.

Lawson has calculated the probable maximum concentrations that might occur on the basis of the observations at Finch, Ontario, and the increase of NTA in detergents which followed the restriction on phosphate content. He concluded that concentrations of up to several parts per million were likely. Since these high concentrations would be associated with unacceptably high contamination with sewage, it is evident that an alternative water supply is the only solution.

National Monitoring Program Groundwater Samples

Seventy-eight samples of municipal drinking water supplies derived from groundwaters were collected from four provinces during the four years of the national monitoring program (Table 15). Of these, only one sample (from a well at Seaforth, Ontario, reported at 50 ppb) was above the detection limit. This is a dubious value, since three previous samples and one subsequent sample were less than 10 ppb.

It is evident that Canadian municipal groundwater supplies which are usually derived from deeper aquifers are not likely to contain significant amounts of NTA.

Special Studies of Shallow Groundwater Situations

Three areas in Canada have been studied intensively by the Department of Fisheries and the Environment to obtain

Table 15. Groundwater Samples

Province	Number of samples examined				Number of samples containing NTA (10 ppb or > 10 ppb)			
	1972	1973	1974	1975	1972	1973	1974	1975
British Columbia	0	11	1	4	0	0	0	0
Saskatchewan	1	1	0	1	0	0	0	0
Ontario	13	14	12	12	0	0	0	1
Quebec	2	2	2	2	0	0	0	0
	<u>16</u>	<u>28</u>	<u>15</u>	<u>19</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>1</u>

information on the mean and maximum concentration of NTA likely to be encountered in this type of situation and to study the mechanisms of the movement of the material into and in the groundwater.

Finch, Ontario

Finch is a small, compact community with a population of 400, occupying an area of less than 1/16 square mile. The inhabitants are served by 114 wells of which 68, chosen at random, were sampled. Sanitary wastes are disposed of via septic tanks and privies. Laundry water containing NTA is disposed of via septic tanks or infiltration to the soil. The relatively shallow overburden of 10-14 feet on the bedrock was not sufficient to prevent NTA from reaching shallow wells, and five out of eight deep wells penetrating the rock showed NTA and/or coliform bacteria which presumably gained access through rock fissures.

In the first sampling, 21 of the 68 wells showed NTA above the detection limits, with concentrations ranging from 15 ppb to 250 ppb. In the subsequent sampling, some of these declined to values of less than 10 ppb, but one in particular (F33), a non-potable well, grossly contaminated with sewage increased to concentrations in the parts per million range (maximum 3.9 ppm). This well and one other similarly contaminated were sampled daily for one month. The first well (F33) fluctuated between 20 ppb and 1,700 ppb with a mean of 30 ppb; the second well (F34) ranged from < 10 ppb to 30 ppb.

Stonewall, Manitoba

Stonewall is in an area of comparatively shallow bedrock (0-17 feet). Twenty-eight wells were sampled; all but one showed less than the detectable limit. The one high value (290 ppb) came from a site where a local source of pollution was identified.

Brandon, Manitoba

Six samples were collected from shallow wells (10-20 feet deep) in glacial lake and spillway deposits. Two

samples contained less than 10 ppb, and the remainder ranged from 13 ppb to 82 ppb. All the wells showed other evidence of sanitary pollution.

Procter & Gamble New York State (Long Island) Study

In 1970-1971, Procter & Gamble sampled the tap water in 129 households in Suffolk and Nassau counties, Long Island (15). This is an area which has a shallow aquifer and has had groundwater problems because of the nature of the wastewater disposal facilities. Individual households used cesspools for sewage disposal and closely located wells for household water supply. In addition, 75 samples were taken at random, many from homes supplied by public utility systems drawing water from a deep aquifer in the area. A number of the shallow wells contained NTA above 25 ppb (the limit of detection at that time), and three samples of water from the public utility systems contained 65-125 ppb.

The number of positive samples occurring suggests that under these undesirable conditions, wells might contain NTA concentrations of 25 ppb or more.

Ontario Municipal Groundwater Supplies

The Canadian monitoring program on NTA in municipal water supplies being carried out by Procter & Gamble includes six municipalities using groundwater. These range in size from a population of 1,600 in Frankford to a population of 51,000 in Guelph. From December 1971 to June 1974, 29 monthly samples have been reported; they are summarized in Table 16 and in a frequency probability plot in Figure 6. Ninety percent of the samples contained 5 ppb or less and the median value was 0.5 ppb.

Guelph—Guelph is the largest city studied. Its water supply is taken from an area of springs, three to four miles east of the city and does not appear to be subject to sanitary pollution. The water is chlorinated before distribution. Twenty of the 29 samples (65%) contained 1 ppb Na_3NTA or less, whereas only two samples exceeded 10 ppb marginally (Fig. 7).

Table 16. NTA in Municipal Groundwaters

Area	Population	Number of Samples	Number of samples in range				Maximum (ppb Na_3NTA)
			0-1	2-5	6-10	10	
Frankford	1,600	29	20	7	2	0	8
Guelph	51,000	29	20	5	2	2	12
Kemptville	2,000	29	13	11	5	0	9
Stouffville	3,200	29	22	7	0	0	5
Stratford	23,000	29	20	7	2	0	8
Uxbridge	2,300	29	22	3	1	3	36
Number of samples		174	117	40	12	5	

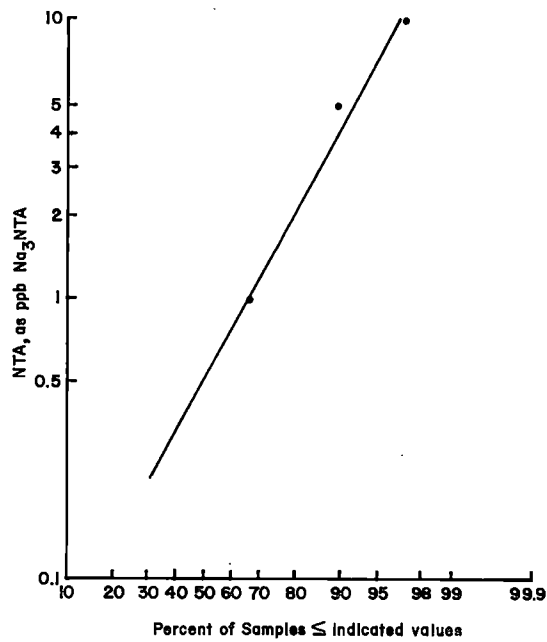


Figure 6. NTA in municipal groundwater supplies (Procter & Gamble data).

Stratford—Stratford is the second largest city with a water supply from deep wells. Twenty of the 29 samples contained 1 ppb Na₃NTA or less and no samples exceeded 10 ppb (Fig. 8).

Uxbridge, Frankford, Stouffville and Kemptville—In Uxbridge, three of 29 samples contained Na₃NTA above 10 ppb (36 ppb, 12 ppb and 14 ppb), but 22 of the samples (76%) were recorded at 1 ppb or less. In the other three towns, no sample exceeded 10 ppb, and 65% of the samples contained 1 ppb or less. Figure 9 summarizes the data.

Conclusions

Private wells are often shallow, imperfectly constructed and located near domestic wastewater and sewage disposal. In villages where wells and sewage disposal facilities are closely associated, drainage from the latter may easily affect neighbouring wells, and NTA levels may be as high as 100–200 ppb. This is usually related to the presence of coliform organisms as shown by Lawson in the Finch study, and the concentration of NTA may vary widely and rapidly.

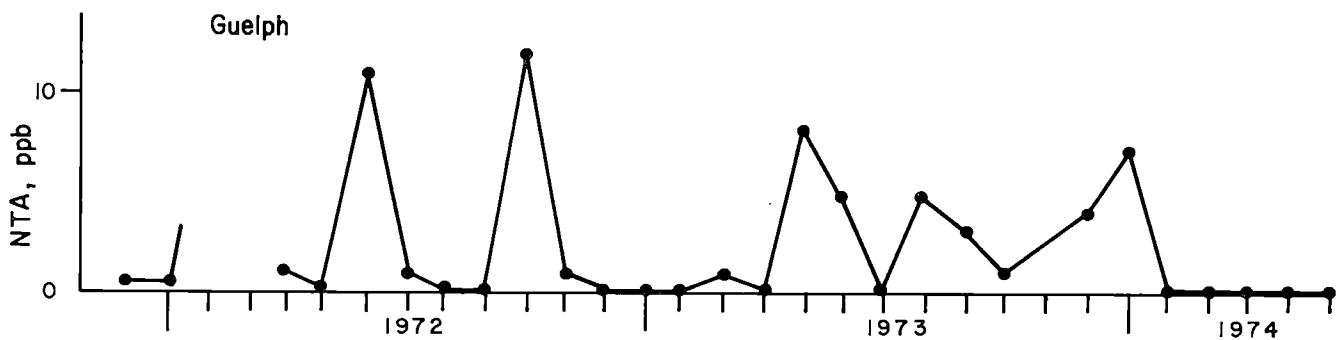


Figure 7. NTA in municipal groundwater supply, Guelph, Ontario (Procter & Gamble data).

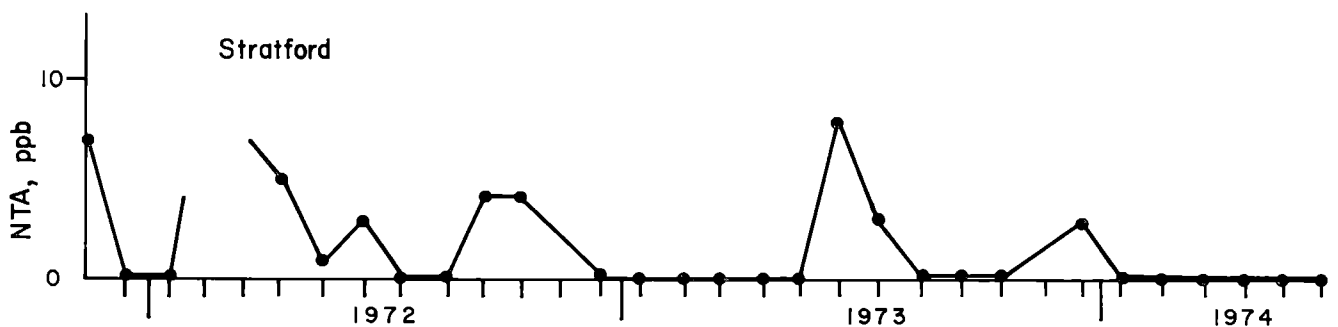


Figure 8. NTA in municipal groundwater supply, Stratford, Ontario (Procter & Gamble data).

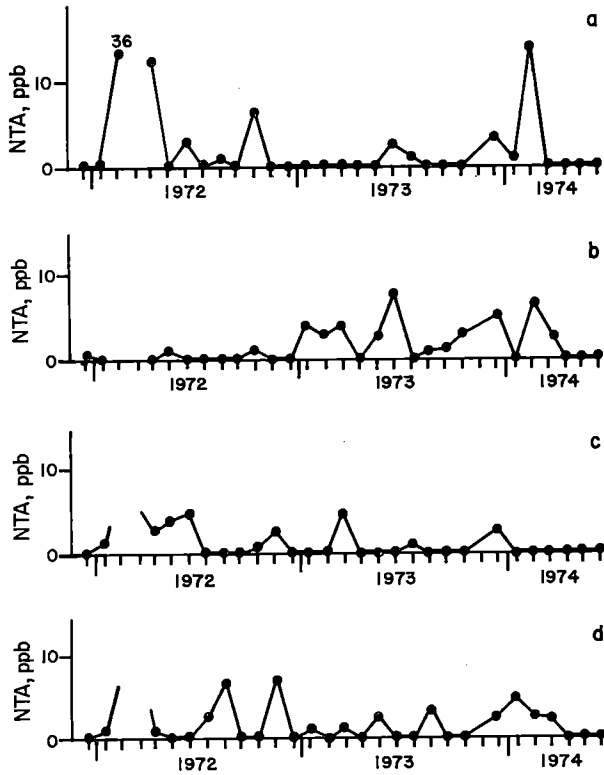


Figure 9. NTA in municipal groundwater supplies of a) Uxbridge, b) Frankford, c) Stouffville and d) Kemptonville, Ontario (Procter & Gamble data).

Municipal groundwater sources are usually better constructed and are well protected from pollution from local sources. Because of the high rates of withdrawal, the drawdown cone in the water table extends considerable distances, and it is possible that water containing NTA might be drawn from long distances. The data mentioned here, however, do not show that this is occurring.

Special Studies

The data collected in Canada by the national NTA monitoring program and from other programs provide information which can be reviewed profitably as special studies. These areas include Hamilton Harbour, a unique situation where large amounts of NTA are discharged in wastewater into a relatively small, isolated bay; the western end of Lake Ontario, which receives the wastewater from two large cities and the inflow from the Niagara River; and the St. Lawrence River system, which carries the outflow from Lake Ontario and receives the wastewater from a number of smaller cities as well as the large input of wastewater from the Montreal metropolitan area.

HAMILTON HARBOUR

Hamilton Harbour provides an unusually appropriate situation in which to observe the performance of NTA in the environment. The Harbour is a relatively small bay, well separated from Lake Ontario since the only connection is a ship canal. The bay receives the runoff from a small watershed of 500 km² and the wastewater from a population of 400,000. The concentrations of NTA observed in the bay water are well within the measurable range, making it much easier to interpret changes than in situations where a large percentage of the samples are at or below the detection level. Furthermore, the bay has been the subject of many studies in the past (16) and its properties and problems are fairly well known.

The physical parameters of concern here are:

Area of watershed	500 km ²
Area of bay	21 km ²
Average depth	13 m
Volume of water in bay	2.8×10^8 m ³
Annual runoff from watershed	1.2×10^8 m ³ /yr
Annual wastewater input (including storm water overflows)	1.1×10^8 m ³ /yr

The annual total water input to the bay, which is 2.3×10^8 m³/yr, is about 80% of the bay volume, and the calculated retention time is thus about 1.25 years. The figures above are quoted from the most recent report on the bay (16) and are appropriate for use in the calculations required here.

Figure 10 is a simplified map of Hamilton Harbour. The major wastewater inputs are from the Hamilton outfall at the mouth of Red Hill Creek and the Burlington outfall in the northeast corner of the bay. Wastewater from Dundas and Waterdown enters the bay after dilution in the tributaries Spencer and Grindstone creeks. Waterdown has only a small population; the wastewater is treated in a small activated sludge plant and a considerable degradation of the residual NTA occurs in the receiving stream (17). The wastewater from Dundas is treated in an activated sludge plant that is presently overloaded. The effluent is diluted by the flow of Spencer Creek and passes through a large area of shallow water (Cootes Paradise) before entering the bay.

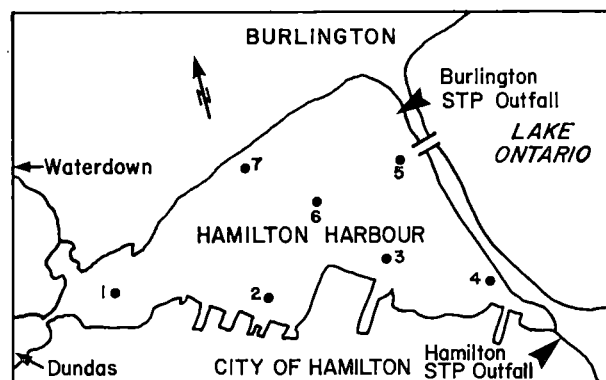


Figure 10. Sampling stations in Hamilton Harbour.

Sampling for NTA determination at seven stations in the bay was begun in December 1971 and has continued on a more-or-less regular monthly basis. Thirty-one sampling runs were used in the following calculations. About midway through the sampling program the secondary (activated sludge) treatment went into operation at the Hamilton sewage treatment plant. The effluent from this plant is the largest single input of wastewater (contributing population of 300,000) and is the predominant source of NTA to the bay. The institution of secondary treatment at Hamilton appears (on the basis of rather limited sampling) to have caused a 75% reduction of NTA input from this source.

Despite the considerable volume of data available in this study difficulty was encountered in the interpretation

because of inherent variability. The details of the study are discussed in Appendix A; only the conclusions are considered here.

1) NTA Input to the Bay

In the period when Hamilton wastewater was receiving primary treatment only, the effluent averaged about 1 ppm NTA (as H₃NTA). The Burlington sewage was receiving secondary treatment throughout the whole period, and it and other smaller sources making up about 25% of the wastewater input probably averaged 0.2-0.3 ppm NTA. Where secondary treatment came into effect in Hamilton, the effluent contained about 0.28 ppm NTA. The institution of secondary treatment at Hamilton therefore reduced the average concentration of the whole flow of wastewater entering the bay from about 0.8 ppm to 0.25 ppm.

2) NTA Level in Hamilton Harbour, before and after the Commencement of Secondary Treatment at Hamilton

It was expected that the reduced input of NTA to the Harbour would result in a reduction in the observed concentrations. A statistical study of each of the seven stations, however, did not show a difference which was significant at the 90% confidence level. This may be because degradation in the bay reduces the NTA concentration to a level just above the detection limit. The variability of individual samples around the mean is so large that a significant difference between the two periods cannot be observed.

3) Effect of Season on NTA Concentrations in the Harbour

To demonstrate a seasonal difference in concentration, the data were examined for each station during two distinct periods: winter (December, January, February and March) and summer (July, August and September). No statistical difference between seasons was demonstrated.

4) Difference between Stations in the Harbour

The average concentrations at different stations were compared and except for station 4, which is closest to the Hamilton outfall, no statistical difference between the stations was demonstrable.

5) Average NTA Concentration in the Harbour

Since a difference between stations and between seasons could not be shown, all of the data from six stations (excluding station 4 which is affected more than the others by its proximity to the Hamilton outfall) were pooled, and a geometric mean (GM) and the range for ± 1 geometric standard deviation (GSD) were calculated. A similar calculation was also made for station 6, separately. The mean and

the range for this station are so close to those of the pooled data that intensive sampling at this one point would have been adequate.

Station	Geometric Mean (ppb)	Range ± 1 GSD (ppb)
Six stations, pooled	14.7	5.5-40
Station 6	16.2	7.0-39

6) NTA Removal in Wastewater Treatment and Subsequent Degradation in the Harbour

The resulting average concentration in the Harbour, assuming steady-state conditions and no degradation in wastewater treatment or in the Harbour, can be calculated from the NTA used by the contributing population and the total water passing through. This is estimated to be 1,100 ppb. If 70% NTA removal occurred in the wastewater treatment the average Harbour concentration would be 330 ppb or 110 ppb if 90% removal was effected.

In comparison with this, if all the wastewater input had the composition of the Hamilton secondary effluent (280 ppb) and was diluted by a slightly larger volume of runoff water, the resultant concentration would be about 125 ppb.

Obviously, further degradation does take place in the Harbour. The Harbour can be considered in a model form as a completely mixed reactor with an input of 100-125 ppb, a retention time of 15 months, a reaction which removes NTA at a constant rate, and an effluent with a composition that is the average concentration in the reactor, i.e., 15 ppb. Its effectiveness in removing NTA may be expressed in terms of the mass of NTA involved:

NTA used by 400,000 population	260,000 kg/yr = 100%
NTA in treated wastewaters	30,000 kg/yr = 12%
NTA in outflow from the Harbour to the lake	3,500 kg/yr = 1.4%

The effectiveness of this "tertiary treatment" resulting from the detention of wastewater plus runoff in the Harbour is evident in protecting the lake from contamination by NTA.

NTA IN WESTERN LAKE ONTARIO

Fourteen sets of samples from seven open-water stations in the western end of Lake Ontario were obtained from December 1971 to December 1973. These data are shown in Table 17 in which the data of samples taken of the Hamilton finished water are also included.

A number of positive samples were found in the lake from December 1971 to July 1972, but after that no values above the detection limit occurred. The earlier sample occurrences, discussed in Appendix B, were studied in detail. It is concluded that these data are erroneous, probably because of accidental contamination, and should be discarded.

Finished waters from ten municipal waterworks on Lake Ontario between Hamilton and Oshawa were sampled on four occasions: November-December 1972, April 1973, January 1974 and March 1975. All of the samples had less than 10 ppb except one from Hamilton (June 1974), which contained 20 ppb, and one from Oshawa (March 1975), which had 10 ppb.

If NTA occurs in the lake water it is probably in the waterworks intakes. Wastewaters discharged into the lake

are retained close to the shore by the effects of the thermal bar and in the coastal jets. Calculations shown in Appendix B, however, indicate that the dilution of even such large volume outflows as those at Toronto is so great that concentrations of NTA approaching the detection level of 10 ppb are unlikely to be found except on rare occasions when an as-yet-undiluted plume of effluent flows directly toward a waterworks intake.

A calculation has also been made in Appendix B to estimate the possible contribution of NTA to the lake by way of the Niagara River inflow. Assuming that NTA was being used at the prevailing Canadian rate in a city the size of Buffalo, New York, and that no degradation occurred in the wastewater treatment, the resultant concentration in the Niagara River flow would be about 3 ppb, well below the detection level. This has been confirmed by five samples taken in August and November 1974 across the mouth of the river which contained less than 10 ppb NTA.

Table 17. NTA in Western Lake Ontario (ppb)

Year	Month	Station							Hamilton finished water
		1	3	4	5	8	9	10	
1971	November								<10
	December	<10	30	10	<10	<10	<10		<10
1972	January	20	160	110	60	30	<10	<10	
	March	<10	<10	<10	<10	20	<10	<10	
	July	30	33	110	<10	<10	<10	<10	
	August	<10	<10	<10	<10	<10	<10	<10	
	September	<10	<10	<10	<10	<10	<10	<10	
	October	<10	<10	<10	<10	<10	<10	<10	<10, <10
	November	<10	<10	<10	<10	<10	<10	<10	
1973	January	<10	<10	<10	<10	<10	<10	<10	
	February	<10	<10	<10	<10	<10	<10	<10	
	March	<10	<10	<10	<10	<10	<10	<10	
	April	<10	<10	<10	<10	<10	<10	<10	<10, <10
	May	<10	<10	<10	<10	<10	<10	<10	
	June	<10	<10	<10	<10	<10	<10	<10	
	October								<10
	November								<10
	December	<10	<10	<10	<10	<10	-	-	<10
	1974	January							
February									<10
March									<10
April									<10
May									20
July									<10
August									<10
September									<10
October									<10

It is concluded therefore that the average concentration of NTA in Lake Ontario water is much less than the minimum detectable level.

ST. LAWRENCE RIVER SYSTEM

The St. Lawrence River was sampled intensively in 1973; three sets of samples were obtained in May, July and September. In addition, the rivers in the Metro Montreal area were sampled once in 1972, 1973 and 1974. The accumulated data are discussed in detail in Appendix C; only a summary of the conclusions is reported here.

Validity of Samples

Of the three samplings on the river in 1973, the July set was anomalous, since it alone contained positive values ranging up to 50 ppb. No sample in the May and September runs had a value exceeding the detectable level of 10 ppb. This situation is discussed fully in Appendix C. Since in general it is not possible to reconcile the higher values with the possible NTA inputs, it is concluded that the July data are invalid and must be rejected. Some of the higher values could be explained by the streaming of effluent flows which tend to follow the near bank of the river they enter for long distances, and dilution of the effluent with the main stream is slow to occur. This is a plausible explanation if the July data *alone* are considered. It is discussed in this way in Appendix C, with the strong reservation that since there is no evidence of this in the May and September samplings, the credibility of the hypothesis is destroyed.

Discussion of Data

For convenience of discussion, the river can be divided into four sections which have different geographical and population-use characteristics.

Lake Ontario to Brockville

The river is in a broad basin and flows in two main channels with many islands. The channels, although fairly well separated, are interconnected at many points, and water may be interchanged between the two streams.

Water entering the river from Lake Ontario is very low in NTA content. The major contributors of NTA to the river are Kingston and Gananoque, but the total amount of NTA used in these cities, with no allowance for treatment-plant or in-stream degradation, is insufficient to produce measurable concentrations in the river after mixing has taken place. The May and September samples do not even indicate the presence of unmixed effluents.

Brockville to Montreal

In this section, the river flows in one channel to Cornwall where it is divided into two channels for a short distance by Cornwall Island. After this it enters Lake St. Francis and discharges into Lac Saint-Louis above Montreal. The major sources of NTA to the river are Brockville and Cornwall; a number of smaller towns between Brockville and Cornwall along the Canadian side also contribute NTA.

In May and September, 34 and 35 samples, respectively, showed NTA at levels of less than 10 ppb, and thus there is no evidence of even undiluted effluent.

Three samples of treated drinking water taken from December 1972 to January 1974 from both Brockville and Cornwall showed no NTA above the detection level.

Montreal Metropolitan Area

This is the only section of the St. Lawrence system where there are substantial occurrences of NTA. River waters and municipal drinking water samples were examined and contained NTA concentrations ranging from less than detectable to 30 ppb. Table C-1 in Appendix C summarizes the data for this area.

The distribution of the positive samples strongly indicates that the pollution of the streams is caused by local wastewater discharges, and the occurrence of NTA in the municipal supplies results from the abstraction of water before degradation and/or dilution have taken place. The increase in the number of positive samples in the period 1972 to 1975 likely is attributable to the expanded use of NTA.

Montreal to the Gulf of St. Lawrence

The water entering this section of the river below the Montreal area is still low in NTA. Three samples taken at Repentigny (at ten-minute intervals) contained 10 ppb in one sample and a less than detectable amount in the other two. There are no large sources of NTA to the river above Quebec City, and all the samples but one (at Sorel one sample out of three contained 10 ppb) are below the detection level. The effect of the wastewater discharge from Quebec City into the large flow of the river is too small to be seen.

Conclusions

The flow of the St. Lawrence River is so large that it is impossible to produce high concentrations of NTA in the averaged and completely mixed flow. Even under the extreme conditions of the total NTA usage by ten

million people being added to the average river flow at Montreal, and allowing for no degradation in wastewater treatment or in the receiving water, the resultant concentration would be only about 30 ppb. Under more realistic conditions where degradation does occur it is unlikely that

concentrations of 10 ppb or more would be produced. If wastewaters are discharged to the river with little or no NTA removal in treatment works higher values may be obtained in water taken for use before complete mixing has taken place.

Current Concerns about NTA in the Environment

Many of the concerns which were expressed initially about the possible effects of NTA in the environment have been resolved by subsequent research. One of the remaining areas of current interest is the possible health effects resulting from the ingestion of small amounts of trace organic substances in drinking water over long periods of time. This concern has been intensified by recently published information indicating a possible relationship between the incidence of cancer in New Orleans and the presence of trace amounts of chlorinated hydrocarbons in Mississippi River water. Attention is therefore being directed toward the small amounts of NTA that may be present in the environment and hence in drinking water. These residues may be subjected to chlorination in several different ways, and potentially toxic compounds could be produced by reaction of chlorine with either the residual NTA itself or with the intermediate products having a transient existence in the biochemical or photochemical decomposition processes. Research already carried out indicates that this is unlikely to occur under environmental conditions.

A second area of present concern is that NTA passing through the environment from its point of use to its ultimate degradation to N_2 , CO_2 and H_2O may cause the mobilization of toxic metals which natural processes would otherwise tend to remove from circulation. The resulting increase in human intake of these metals over a long period of exposure may have significant health effects.

The questions requiring more research now are:

- a) what substances are produced in the biological or photochemical degradation of NTA;
- b) what concentrations of NTA, its degradation products and chelated metals may be expected; and
- c) at what concentrations are these likely to have significant effects with respect to public health, bearing in mind that similar degradation products and other chelators are present in natural waters from purely natural sources.

Definitive answers to these questions must come, quite evidently, from highly specialized research. This is beyond

the scope of this paper, but it is important to point out that problems associated with NTA and its products should be considered in a proper relationship with other substances occurring naturally.

CHLORINATION OF NTA

NTA and its degradation products may be subjected to chlorination in several situations in connection with their use and disposal.

Chlorination in Laundry Use

In laundering, relatively high concentrations of NTA and hypochlorite are brought together at elevated temperatures for short periods of time. Monsanto research (18) indicates that under these conditions, however, the NTA which is bound with calcium or magnesium does not react with chlorine, and the unbound NTA and any intermediate products are oxidized to N_2 , CO_2 and H_2O .

Wastewater Effluent Chlorination

Chlorination of secondary effluents is commonly required by public health authorities as the final disinfection step in wastewater treatment. Chlorinated effluents are known to be highly toxic to aquatic organisms, particularly certain fish, even after considerable dilution. Chemical dechlorination reduces the toxicity, but very complete dechlorination is necessary to avoid long-term effects. Some fish are sensitive to residuals as low as 0.01 ppm.

The chlorination of NTA under conditions existing in wastewater treatment has been studied in a preliminary way by Monsanto. Small amounts of chlorinated aminoacids are produced as intermediate products. They are slowly degraded in the environment and thus may make a contribution to the toxicity of chlorinated effluents.

The chlorination of wastewater effluents is a complicated matter for which detailed information is very scarce. More work needs to be done to identify the reaction products produced in the presence or absence of added NTA, considering that many of the intermediate products of the biological degradation of proteins in normal sewage

are similar to or identical with those produced from NTA and may come from a much larger source in wastewater than the added NTA.

The stability of chlorinated products, especially those having carbon-chlorine bonds, is important to dechlorination by the intentional addition of dechlorinating chemicals (SO₂) or by natural photochemical processes in receiving waters. The immediate acute toxicity of chlorinated amino substances may be removed readily by chemical dechlorination, leaving the less reactive chlorine-carbon bonded substances unreduced. It is this latter group that are considered to have the greater potential for carcinogenicity.

Chlorination of Cooling Water

To avoid the build-up of slimes on heat exchanger surfaces the large volumes of cooling water which are required in power generating stations are subjected to intermittent heavy chlorination. Since the waters may be clean and low in ammonia, high residuals of free chlorine are produced which have a greater potential to react with trace amounts of NTA than similar doses of chlorine added to effluents in wastewater chlorination. NTA, however, is likely to be present in such waters in much lower concentrations than in effluents.

Chlorination of Drinking Water

This is the point at which chlorinated NTA products may be produced and consumed by man with little detention time or opportunity for decomposition or dilution. It is expected that NTA concentrations in raw waters will be relatively low as the result of degradation in wastewater treatment plants and degradation and dilution in receiving waters. (An exception might be when groundwaters contaminated by NTA are chlorinated.)

The chlorination method presently preferred in water treatment, because of its bactericidal effectiveness, is free-residual chlorination, which implies that sufficient doses of chlorine are applied to destroy chloramines and concentrations of free chlorine in the order of 2-10 ppm are maintained for several hours. This results in the complete oxidation of ammonia and various taste- and odour-producing substances as well as providing good bacterial removals. As the last stage in treatment the residual may be reduced, if necessary, to an acceptable level for consumption by dechlorination with sulphur dioxide.

The Monsanto report suggests that NTA in raw water is affected little, if at all, by chlorination as practised in normal purification where the concentration of both reactants is low. NTA in the raw water is thus passed through the treatment plant and appears in the finished water without much loss.

Activated carbon, which is used in powdered form or as beds of granular carbon through which water is passed, is used in water purification to remove taste- and odour-producing substances. There is some evidence, previously discussed, that this treatment may remove NTA or its chlorinated products. In view of the current interest in the effects of trace organics and particularly of chlorinated organics in drinking water, the more general use of carbon in water treatment could be justified as an additional health safety measure even when it is not required for improving the organoleptic properties.

MOBILIZATION OF TOXIC METALS

Because of its chelating properties, NTA has the potentiality of rendering metals soluble that otherwise would form insoluble precipitates and be removed from waters by sedimentation under natural conditions or in water treatment. These solubilized metals would then be more available for incorporation in the food chains and in addition, might be presented to man in undesirably high levels in drinking water.

The existence of NTA in its free or chelated forms depends on the stability constants of the metal chelates, the concentration of metal ions available for reaction and the pH of the water. If NTA is in short supply there will be a competition among the metals, the outcome of which is determined by the stability constant of the NTA metal chelate and the metal concentration. The equilibrium established is dynamic and changes as the availability of metals and the concentration of NTA vary.

The opportunities for mobilizing metals occur in several situations:

- a) In laundering use, where the concentration of NTA is high and the abundant cations are calcium, magnesium and iron.
- b) In wastewater treatment. The concentration of NTA in the influent wastewater is about 10 ppm, and toxic metal concentrations are low unless specific industrial wastes are present. It has been shown that the NTA chelated with certain heavy metals is resistant to biodegradation, and consequently the NTA contained in effluents may be made up largely of these resistant chelates.
- c) The solution of metals from river and lake sediments. The concentration of NTA in the lake or river water is likely to be very low (as the result of degradation and dilution) and the contact of the contained NTA with the insoluble metal compounds is limited by

diffusion rates unless there is mechanical mixing by water turbulence. Metals present in recently deposited industrial waste sediments are known to be more easily extracted than those in deposits of natural materials.

- d) The process of precipitation of metals by natural processes in receiving waters. This may be inhibited by the solubilizing effect of small concentrations of NTA. Unchelated NTA is not likely to be present in natural situation, and NTA contained in wastewater effluents is already chelated with calcium, magnesium and metals, and particularly with iron, which is relatively abundant and has a chelate of high stability.

The importance of heavy metals in a direct health effect depends on the concentration existing in raw water and the effects of treatment processes. A state of dynamic equilibrium exists between chelated and unchelated forms. Some amount of free NTA and free metal ions exists in equilibrium with the chelate. The free NTA is subject to biodegradation, especially in systems that are so dilute that the toxicity of the free metal ion does not interfere. Chau and Shiomi have shown that the addition of

small amounts of NTA (1 ppm or more) to natural waters and stirring with the existing sediments will result in an increase in the soluble metal concentration in the water phase. This returns to the original level quite quickly when the free NTA is degraded.

CONCLUSION

It is concluded therefore that under normal environmental conditions, the effects on metal uptake of the residual NTA concentrations that are likely to happen will be negligible and are not likely to be demonstrable against the normal variations in metal concentrations.

The abnormal situations in which significant mobilization might occur would include:

- a) wastewater effluents from plants having large inputs of toxic metal salts from industrial wastes and
- b) the discharge of untreated or poorly treated municipal effluents (containing a high concentration of NTA) into receiving waters to which industrial wastes containing soluble or insoluble metal salts are discharged.

Conclusions and Recommendations

CONCLUSIONS

The results of the national monitoring program are:

- 1) NTA has not accumulated in surface waters as a result of its expanded use in Canada. Rapid biodegradation takes place in the common aerobic wastewater treatment processes and continues in the receiving waters.
- 2) The nation-wide survey of municipal drinking waters, which has now extended over four years, shows relatively few cases where NTA occurs above the detection limits. Where higher values exist the raw water is polluted with wastewater containing NTA and is abstracted for use before sufficient dilution and degradation can take place.
- 3) In groundwaters, degradation under the prevailing anaerobic conditions is slower and higher levels of NTA are observed in waters from aquifers which are grossly polluted. This problem occurs locally where a shallow aquifer receives drainage from septic tanks and soakage pits.
- 4) Municipal water supplies derived from groundwater show little evidence of pollution by NTA.

RECOMMENDATIONS

The monitoring program shows that NTA in receiving waters in Canada is not a widespread problem, if it is a problem at all. Continuing the program in its present form will not provide much more information. More concentrated attention should be directed toward specific areas which have been shown by the present surveys to be sensitive. Where large amounts of NTA are discharged and where the receiving waters are reused for water supplies before sufficient time for degradation elapses, large populations may be exposed to an unavoidable NTA intake.

The following specific areas are suggested for further investigation.

Sewage Treatment Plants

A detailed study of the removal of NTA by a large standard sewage treatment plant should be undertaken. A large plant is important, since it handles a large daily flow of NTA, the operating conditions are different from those in small plants, and the effluent from a large population is discharged to the receiving waters as a point source. Winter temperature conditions are less severe in a large plant, and the reduction in the efficiency of NTA removal exhibited by small plants in winter may not appear as important.

Good information on sewage treatment plant performance would make it possible to calculate accurately the maximum possible concentrations of NTA in the receiving waters.

Degradation of NTA in a Receiving Stream

Intensive study should be done on the degradation of NTA in a receiving stream. Most of the information available at present concerns small streams where detention times, re-aeration and bottom-to-volume ratios are much different from those in larger rivers. The small amount of information concerning the fate of NTA in larger rivers is too limited to be useful.

The Grand River would be a suitable study area. There are a number of inputs of NTA that can be quantified, and streamflow data are readily available. The areas studied should include the dilution ratios available, with seasonal variations; the in-stream degradation, as affected by temperature, loading, biological activity in the stream; degradation affected by indigenous bacteria or bacteria added in effluents; the effects of chlorinated effluent addition on degradation of existing NTA burden; and the effect of bottom organisms on degradation rate.

Degradation of NTA in Lakes

Degradation in lakes is somewhat different from that in streams; the detention period is long, the bacterial populations are different in concentration and activity, and with greater water clarity and greater depths, the photochemical effects of light may be more important. Special attention should be directed to determine the relative effectiveness of

biodegradation and photochemical decomposition in reducing the concentration of NTA in the lakes situation. The intermediate products of photochemical degradation may be significant because of higher yields, greater persistence and consequently the possibility of entering into subsequent reactions (19).

NTA in Water Purification Plants

It is generally assumed that water purification plants do not remove substantial amounts of NTA because of the ineffectiveness of the usual chemical processes involved, the very small amount of biological activity that can be present, and the short detention time that is available. Yet there is some evidence presented here that shows the NTA con-

centration in treated water may be significantly lower than that in the raw source water.

There are two processes that could be effective in making substantial reductions in NTA concentrations: a) free-residual chlorination, where free-chlorine residuals of several parts per million are maintained for two to four hours and b) activated carbon, which is used primarily for taste and odour removal.

A plant of moderate size, which uses a raw water supply that regularly contains NTA and which employs one or both of these treatments, should be selected and studied intensively.

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Hamilton Harbour

The following is the result of a detailed study of the Hamilton Harbour NTA data, which has been mentioned in Chapter 3. The calculations have been made using the data up to November 1974. Data for three more months became available later (shown in Table A-1), but would not affect the conclusions significantly.

HAMILTON HARBOUR STUDY

Hamilton Harbour provides an unusually appropriate situation in which to observe the performance of NTA in the surface water environment. While the situation is unique in its applicability, it does not necessarily represent the typical situation into which wastewaters containing NTA are discharged. Yet since the concentrations actually found are in the measurable range, the phenomena involved can be seen more clearly than in another environment where a much larger percentage of the samples are at or below the detection limit.

Hamilton Harbour is a land-locked bay connected to Lake Ontario by a relatively narrow ship canal. The bay receives the precipitation runoff from a small watershed plus the treated municipal wastewater from a population of about 400,000, and a variety of industrial wastes from a number of industries among which the primary and secondary steel industries predominate. The bay has also been the subject of many studies in the past.

Sampling for NTA began at seven stations in Hamilton Harbour in December 1971, and has continued at more-or-less regular monthly intervals until the present time. Data were available from 31 sampling runs for this study. About midway through this sampling program secondary (activated sludge) treatment came into operation at the Hamilton sewage treatment plant. The Hamilton effluent is the largest single input and the predominant source of NTA in the bay; the institution of secondary treatment at Hamilton resulted in what appears to be a 75% reduction of input from this source, based on a very limited amount of sampling.

Serious problems are involved in the study of the available data and limit the conclusions which can be

drawn. Yet in spite of these, important and useful information can be extracted. They are discussed in detail later.

The study was directed to determine the following:

- a) whether the reduced input of NTA to the bay, following the institution of secondary treatment, resulted in a lower concentration in the bay water,
- b) whether a seasonal change in concentration of NTA in the bay water could be observed,
- c) whether concentrations at the individual sampling stations were significantly different, and
- d) whether a reliable estimate of the rate of emission of NTA from the bay to the lake could be made.

No change in concentration of NTA in the bay water could be detected after the institution of secondary treatment at Hamilton because the average concentration (expressed as the geometric mean) is low (approaching the level of detection) and the variability is so large that a difference great enough to be significant is not observed.

A study of the concentrations observed in the winter and summer months did not show a significant difference.

Significant differences between pairs of stations (excluding station 4) could not be demonstrated. This indicates that over relatively long periods of observation (i.e., months), the open-water stations can be regarded as representative of a single population and the data from them can be pooled.

Using all the data from the six stations, a reliable estimate of the average concentration in the bay can be made. The geometric mean (GM) of all these samples is 15 ppb and the range including ± 1 geometric standard deviation (GSD) is 4.4-53 ppb. This average value, multiplied by the amount of water passing through (which is approximately equal to the outflow to the lake), gives an average emission rate of 3,500 kg H₃NTA per year, considered over a long-time scale. This emission rate per day is 10% of the

Table A-1. Summary of NTA in Hamilton Harbour Samples (ppb)

Year	Month	Period	Station							
			1	2	3	4	5	6	7	
1971	December	"b"	20	15	25	60	20	10	20	
1972	January		5	5	40	40	20	20	5	
	February			(40)	(70)	(10)	(90)	(140)	(140)	
	March		70	50	30	110	80	50	30	
	July		130	60	40	100	5	5	5	
	August		90	5	60	80	5	50	5	
	September		5	5	5	40	5	50	5	
	October		5	5	10	110	20	5	5	
	November		5	5	80	110	5	10	5	
	December		5	5	20	40	5	20	5	
1973	January		20	5	5	5	10	20	20	
	March		30	30	30	40	10	30	30	
	April		70	50	70	350	70	60	70	
	May		5	5	5	100	20	5	5	
	June		5	10	10	130	10	10	20	
	July		10	5	10	90	10	20	10	
	1973	August	"a"	10	5	10	10	5	20	5
September			5	20	5	30	20	5	5	
October			10	5	10	60	10	10	5	
November			30	10	20	90	20	10	10	
December			5	5	20	100	5	5	20	
1974	January		30	30	30	70	40	20	30	
	March		40	60	80	110	80	70	90	
	April		40	60	80	80	80	100	60	
	May		20	30	30	70	50	20	40	
	June		5	5	5	140	20	5	5	
	July		5	20	30	20	20	10	10	
	August		5	20	40	40	20	10	5	
	September		10	10	5	20	30	20	20	
	October		5	5	10	20	5	10	10	
	November		50	20	80	160	40	30	60	
	December		10	5	20	40	30	30	20	
	1975	January		20	40	20	160	10	10	20
		February		30	30	40	50	50	20	20

estimated daily input to the bay through treated wastewater discharges and is 1.3% of the estimated NTA consumption by the tributary population.

The major wastewater inputs are from the Hamilton outfall in the mouth of Red Hill Creek and the Burlington outfall (Fig. 10). Wastewater from Dundas and Waterdown enters the bay after dilution in the tributaries Spencer and Grindstone creeks. Waterdown has only a small population; the wastewater is treated by an activated sludge plant and considerable degradation of remaining NTA occurs in the receiving stream (17). The wastewater from Dundas is treated by an activated sludge plant which is presently overloaded. The effluent passes through a large area of shallow water (Cootes Paradise) before entering the bay.

The physical parameters of concern here are:

Area of watershed	500 km ²
Area of bay	21 km ²
Average depth of bay	13 m
Volume of water in bay	2.8 x 10 ⁸ m ³
Runoff from watershed	1.2 x 10 ⁸ m ³ /yr
Wastewater input (including storm water overflows)	1.1 x 10 ⁸ m ³ /yr

As previously mentioned, the annual total water input to the bay, 2.3 x 10⁸ m³/yr, is about 80% of the bay volume. The calculated retention time in the bay is thus about 1.25 years. The data above are quoted from a recent report by the Ministry of the Environment from a study of Hamilton Harbour (16) and are appropriate for the calculations to be used here.

INTERPRETATION OF THE DATA

It is important to appreciate the difficulties encountered in interpretation of the present data to avoid drawing erroneous and unwarranted conclusions.

In the study published by the Ministry of the Environment it was emphasized strongly that the motion of water in the bay and the flows in and out of the ship canal are very complex and cannot be represented accurately by any simple pattern. The water quality observed at any one point in the Harbour and any particular point in time not only is the result of the waste inputs and the reactions proceeding in the bay but also is affected by water currents caused by wind action and by sustained oscillations in the bay. As a result of the oscillations, the thermocline may vary up and down over a wide range. Changes in the lake level resulting from lake oscillations control the flow of water in and out of the canal on the short-term basis.

Because of the relatively short period of the bay oscillations, any sampling cruise of two hours duration cannot be considered to be synoptic and the data obtained do not represent the condition prevailing at any one time. Thus the individual values found at any station at any particular time cannot be interpreted precisely since they are the results of many unknown factors, some of which may be changing rapidly. If the bay is sampled over a long period of time it may be considered to be "well mixed," although this is definitely not so over short periods of observation.

Accordingly, the best interpretation that can be made is obtained by grouping the data appropriately to represent particular conditions or situations, and then by accepting the observed values as the results of random sampling under the circumstances defined by the grouping.

This method of interpretation is further limited by the relatively small number of samples that are usable after grouping and the high degree of variability that is observed. Yet if significant differences between groups cannot be demonstrated the pooling of data from two or more groups can be justified, and thus the larger number of samples made available can be used to advantage.

Log-Normal Distribution

The first approach in this study was made on the basis of using arithmetic means and standard deviations. This is usually the first approach, but since on further study a log-normal distribution was found in the data, the use of the arithmetic mean and standard deviation was rejected as being inappropriate and misleading.

The frequency distribution for the data from some selected stations is shown in Figure A-1. A straight-line relationship on log frequency paper is quite evident even though the number of data points is very low. If all the data from the six open-water stations are pooled (and this is justified, as will be shown later), the frequency distribution plot in Figure A-2 confirms the log-normal distribution. Thus for this report, the data of each individual point were log-transformed before calculating the mean and the standard deviation. To distinguish these values, they are referred to as the geometric mean and the geometric standard deviation.

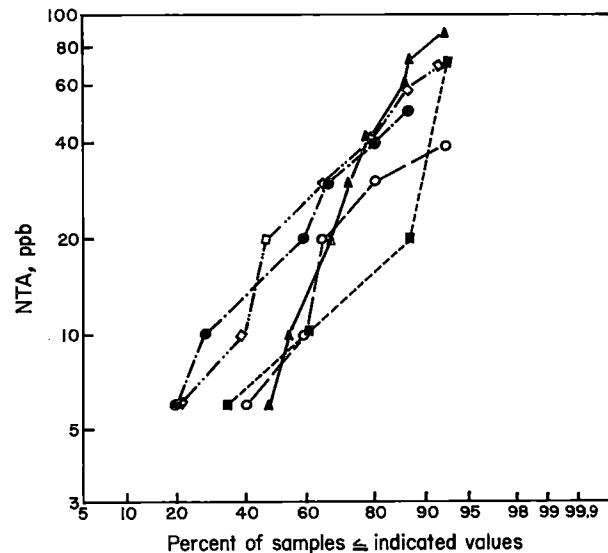


Figure A-1. Frequency distribution of NTA in Hamilton Harbour, four individual stations.

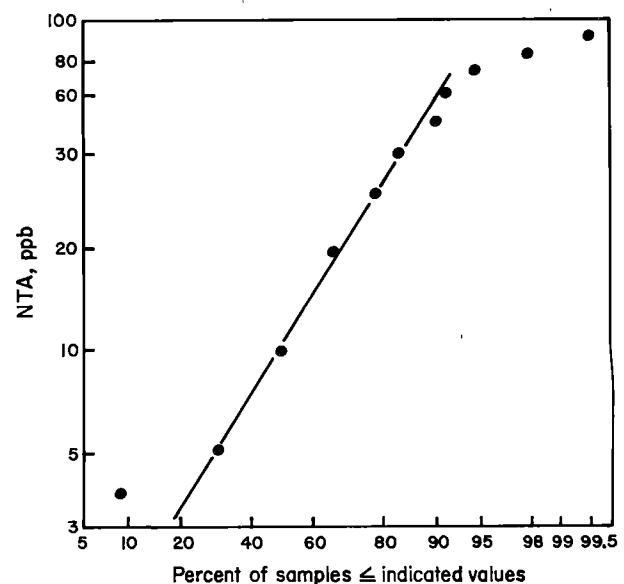


Figure A-2. Frequency distribution of NTA in Hamilton Harbour, six stations pooled.

The appropriateness of the assumption of a log-normal distribution is illustrated by this sample calculation which uses data for station 1 during the "b" period (before secondary treatment), referred to below. There are 15 data points which range from <10 ppb to 130 ppb.

Arithmetic mean	32 ppb
Standard deviation (SD)	39 ppb
Range for ± 1 SD	-7 to 71 ppb
Range for ± 2 SD	-46 to 110 ppb
Geometric mean	15 ppb
GSD (usable only in log form)	
Range for ± 1 GSD	4.35 to 53 ppb
Range for ± 2 GSD	1.25 to 184 ppb

The arithmetic mean is a figure which is highly influenced by a single individual high value. The range for ± 1 SD or ± 2 SD includes negative numbers and is meaningless in this context.

HAMILTON HARBOUR DATA

Table A-1 summarizes all of the Hamilton Harbour data. In this Table, values reported as less than 10 ppb, the limit of detection, were tabulated arbitrarily as 5 ppb in order to have a number to be used in calculations. Thirty percent of all the samples were reported as less than 10 ppb and 20% as 10 ppb. It is reasonable to assume that those reported as less than 10 contained some NTA. The value of 5 ppb was chosen as being probably close to a real value. (Using 1 ppb instead of 5 ppb reduces the geometric mean appreciably. For example, for the data of station 6 in which six out of 30 samples were reported as less than 10, substituting "1" in place of "5" gave a geometric mean of 11.7, as compared with 16.2 for the former.)

In Table A-1, data are shown for February 1972 in parentheses. These are valid data, but were not used in the calculations since data for February of other years were not available.

EFFECT OF REDUCED NTA INPUT

The data of Table A-1 were examined to determine whether the commencement of secondary treatment at the Hamilton sewage treatment plant affected the concentration of NTA at any or all of the bay stations.

The NTA concentrations observed in the relatively few samples of Hamilton effluent (24-hour composites, taken one day per month) are shown in Figure A-3. A marked change is evident after secondary treatment started. The average concentration in the period before treatment was about 1.0 ppm. After the secondary plant was in operation the NTA concentration declined to 0.2-0.3 ppm, and the variance was much less. The mean of seven samples in this period was 0.28 ppm, with a standard deviation of 0.065 ppm.

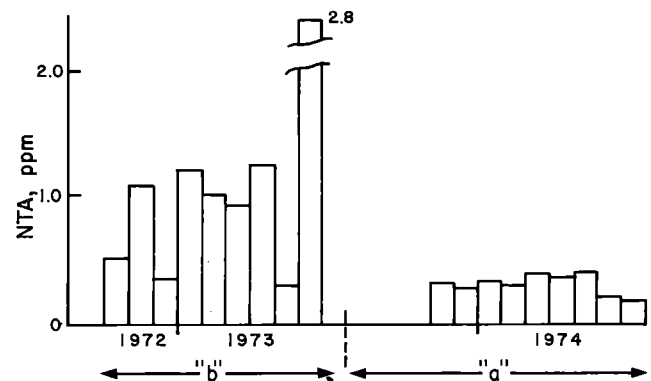


Figure A-3. NTA in the effluent from the Hamilton sewage treatment plant. Period "b" is before secondary treatment; period "a" is after secondary treatment.

This sudden and substantial change in NTA input would be expected to result in a noticeable change at some of the stations, particularly at station 4 which is the most directly influenced by the Hamilton effluent.

Table A-2 compares the geometric means at each station for the periods "b" and "a" (after secondary treatment was in effect). These data are shown graphically in Figure A-4. A t-test performed on the means for each

Table A-2. NTA in Hamilton Harbour Stations in Periods "b" and "a" (GM)

	Station						
	1	2	3	4	5	6	7
Period "b"	15.2	12.6	19.9	68.4	12.5	17.5	10.5
Period "a"	12.3	14.0	19.8	51.7	20.8	15.0	15.1
t-Test	0.530	0.928	0.017	0.868	1.526	0.488	1.031

Note: t represents 28 degrees of freedom
90% confidence level critical t = 1.67

Table A-3. NTA in Hamilton Harbour, Winter and Summer Periods

Station	Geometric mean		T (as ln)	Difference
	Winter	Summer		
1	17.1	12.5	0.588	no
2	14.3	11.3	0.509	no
3	25.4	14.9	1.270	no
4	49.0	37.3	0.665	no
5	18.5	10.5	1.313	no
6	21.1	15.4	0.808	no
7	19.9	6.8	3.10	yes
Six stations (excluding No. 4)	19.1	11.5	2.895	yes

Note: t represents 16 degrees of freedom
95% confidence level critical t = 1.74

station did not show any significant difference between the two periods at any station. The t-values, also shown in Table A-2, indicated that the most nearly significant difference occurred at station 5, which is the station most influenced by currents in and out of the canal.

examined for each station in two periods which were distinctly different: winter (December, January, March) and summer (July, August, September). The data for February 1972 were not included since similar data for 1973 and 1974 were not available.

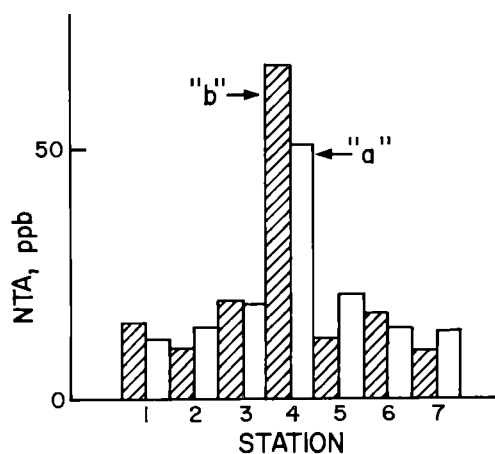


Figure A-4. NTA in Hamilton Harbour before and after secondary sewage treatment, by stations.

Since no significant difference can be shown between the two periods, it is justifiable to combine the data.

Figures A-5 and A-6 show the distribution of NTA in the Harbour in the periods "b" and "a". As mentioned, there is no statistical significance between pairs of stations, excluding station 4 which is the nearest to the Hamilton outfall.

EFFECT OF SEASON ON NTA CONCENTRATIONS IN THE HARBOUR

To demonstrate a seasonal difference in the concentration of NTA in the Harbour samples, the data were

The data for each station are summarized in Table A-3 and shown in Figure A-7. At every station the concentration was higher in the winter period, but for all stations

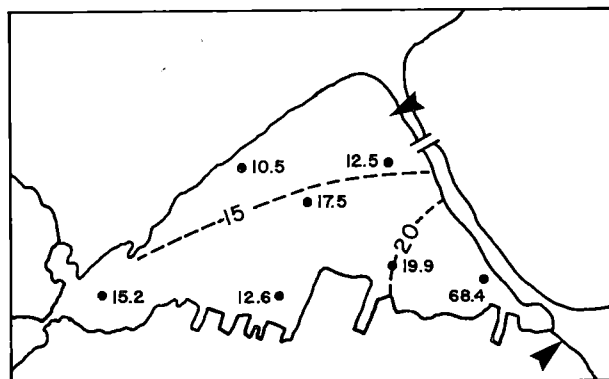


Figure A-5. Geometric mean of NTA in Hamilton Harbour for period "b".

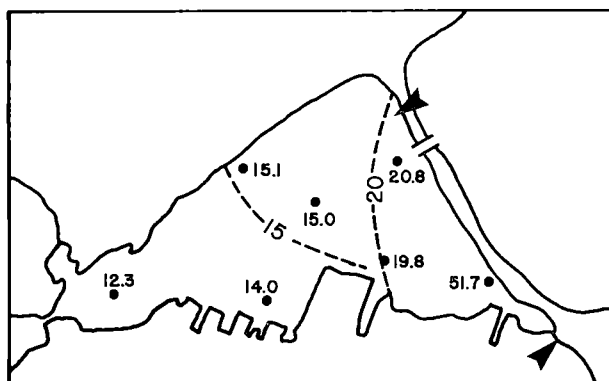


Figure A-6. Geometric mean of NTA in Hamilton Harbour for period "a".

except station 7 the difference was not significant. When the data of the six stations (excluding station 4) were pooled, the winter average of 19 ppb was reduced to 11.5 ppb in summer, and this difference is significant.

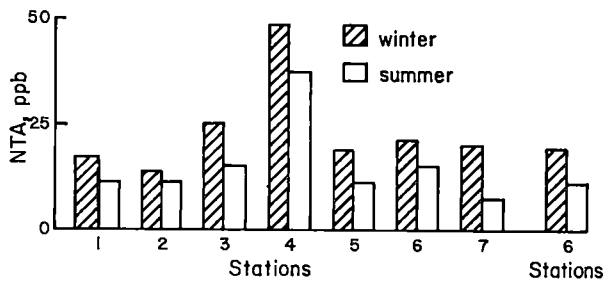


Figure A-7. Comparison of winter and summer geometric means of NTA in Hamilton Harbour.

SIGNIFICANCE OF DIFFERENCE BETWEEN STATIONS

The significance of the differences in geometric means between selected Harbour stations was investigated by using the t-test on all the data available for each station. Table A-4 shows the geometric means of 30 samples at each station. The t-test was performed on the pairs marked by arrows, and in all of the cases the differences were not significant at the 90% level.

Table A-4. NTA in Hamilton Harbour, Geometric Means of 30 Samples at Each Station

Station :	1	2	3	4	5	6	7
Geometric Mean :	14	12	20	59	16	16	12.5

Arrows in the original table indicate comparisons between stations 1-2, 1-3, 1-5, 1-6, 1-7, 2-3, 2-5, 2-6, 2-7, 3-5, 3-6, 3-7, 5-6, 5-7, 6-7.

Accordingly it is justifiable to pool the data from the six stations (excluding station 4) to obtain a mean concentration of NTA in the whole bay for the period of observation. This yields a geometric mean for 180 samples of 14.7 ppb; the range of ± 1 GSD is 5.5-40 ppb. This in turn was compared with the geometric mean for station 6, 16.2 ppb, and the range of ± 1 GSD, 7-39 ppb. The difference between the two means is not significant ($t = 0.503$). Figure A-8 shows the geometric means for all stations using all samples.

CALCULATION OF NTA INPUT TO THE HARBOUR

The input of NTA to the Harbour can be calculated from the Canadian per capita consumption of detergents,

the average NTA content of detergents sold in Canada as furnished by Procter & Gamble and the size of the contributing population. Combining the NTA input calculated in this manner with the total water flow to the Harbour (waste effluents, runoff, tributary, etc.) leads to an average concentration of 1,100 ppb in the Harbour water.

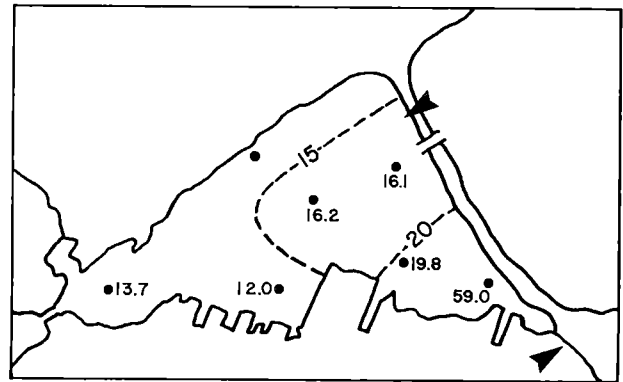


Figure A-8. NTA in Hamilton Harbour, geometric means for all samples.

In comparison with this, the effluent from the Hamilton plant averaged 280 ppb (Fig. A-3). If the balance of the wastewater input, as estimated by the Ministry of the Environment, was of the same composition and if this was diluted by somewhat more than an equal volume of runoff, the average concentration in the Harbour would be 125 ppb.

Further degradation of NTA from these calculated levels takes place in the Harbour. The bay can be considered in a model form as a completely mixed reactor with an input as calculated above; a retention time of 1.25 years; a degradation reaction continuously removing NTA; and an outflow composition which is the average composition of the bay, i.e., about 15 ppb. (On a short-term basis, the bay is obviously not completely mixed as shown by the high and low values obtained in sampling, but over a longer time scale complete mixing is a valid assumption.)

OUTPUT FROM THE HARBOUR

On the basis of the argument above, the output of NTA from the Harbour over a long-term scale is the volume of the water passing through multiplied by the average concentration. This is calculated to be 3,500 kg H_3NTA per year. This is about 10% of the amount put into the Harbour by way of wastewater inflows and 1.3% of the 260,000 kg NTA used annually by the population contributing wastewater to the Harbour.

**CALCULATION OF HARBOUR NTA
INPUT AND OUTPUT**

H₃ NTA population of 400,000:

$$0.65 \text{ kg/capita/yr} \times 4 \times 10^5 = 260,000 \text{ kg/yr}$$

H₃ NTA to the Harbour via wastewater flow:

$$1.1 \times 10^5 \text{ m}^3/\text{yr} \text{ at } 280 \text{ ppb} = 30,000 \text{ kg/yr}$$

H₃ NTA outflow to lake:

$$2.3 \times 10^8 \text{ m}^3/\text{yr} \text{ at } 15 \text{ ppb} = 3,500 \text{ kg/yr}$$

Western Lake Ontario

Sampling for NTA at seven stations in the open water of the western end of Lake Ontario was begun in December 1971. On the first four sampling trips a number of samples contained NTA well above the detection level.

In the following ten sampling trips, however, no values of NTA were found at or above the detection level. NTA has not been found above detectable levels at any of the waterworks intakes from Hamilton to Oshawa (except for one value of 20 ppb at Hamilton, June 1974, and a value of 10 ppb at Oshawa in 1975) despite that over this period from 1972 to 1975 the per capita usage of NTA increased by 2.5 times. The most recent sampling in Lake Ontario, in January 1975, included 35 samples from the Canadian side of the lake and none contained NTA at or above 10 ppb.

It was therefore necessary to examine the earlier data to determine whether they were valid and represented the actual situation or whether another explanation should be sought.

The data for the sampling in January 1972 are shown in Figure B-1. They can be interpreted readily as representing a plume emitted from the Toronto metropolitan area (the largest source of NTA to Lake Ontario) and carried by the counter-clockwise circulation pattern toward Hamilton and Grimsby. As the current approaches the Niagara River NTA is diverted toward the centre of the lake, the two easterly samples of the group showing levels of less than 10 ppb.

The data of the July 1972 sampling may be interpreted similarly, but the pattern is less well developed (Fig. B-2).

The objections to this interpretation are threefold:

- a) The total mass of NTA existing in the lake in January is unrealistically large. The calculation is shown below. It can be seen that the minimum quantity of NTA necessary to account for the increase in NTA mass from December to January, a *one-month* period, represents a *three-month* total output from Metro Toronto with no allowance for degradation or dilution beyond a 1-m depth.
- b) In the ten sampling trips after July 1972, no values of 10 ppb or more were found in any of the lake samples. Also, NTA has not occurred at levels above

10 ppb in 30 samples from the municipal waterworks between Hamilton and Oshawa (except one sample of 10 ppb from Oshawa in 1975 and one sample of 20 ppb out of a total of ten taken at the Hamilton waterworks in 1974). This apparent scarcity of positive samples in latter years has happened even though NTA consumption in Canada has increased 2½-fold.

- c) In a general sampling of the Canadian half of Lake Ontario in 1975, no sample of the 35 taken had an NTA level equal to or above 10 ppb.

It is concluded therefore that the data from the four earliest sampling trips are invalid and the concentration of NTA in the lake is, and always has been, below the detectable limit of 10 ppb, except possibly in the immediate vicinity of large outfalls.

CALCULATION OF NTA IN LAKE ONTARIO JANUARY 1972

Toronto wastewater effluents represent by far the largest possible sources of NTA to Lake Ontario. The contributions from other lakeshore cities are small in comparison, and as shown in Appendix A, the input from Hamilton after tertiary treatment in the bay is negligible. The pattern of the distribution of NTA in the lake in January 1972, as shown in Figure B-1, appears to be consistent with a large input from Toronto. The following calculation was made to determine whether the Toronto effluent could account for the mass of NTA which apparently was present in the lake on that occasion.

Referring to Figure B-1, the NTA level in the lake samples is high (110 ppb and 160 ppb) at the stations near Toronto sewage treatment plant outfalls. The sewage effluent is decidedly warmer than the lake water in January; therefore, it may be assumed that it rises to the surface and spreads over the quiescent lake in a layer 1 m deep. The area of the triangle shown on Figure B-1 (825 km²) is approximately the area which is covered by this layer of effluent containing NTA; an average concentration of 30 ppb over the area is reasonable. The mass of H₃NTA present in the lake in this film is thus 25,000 kg.

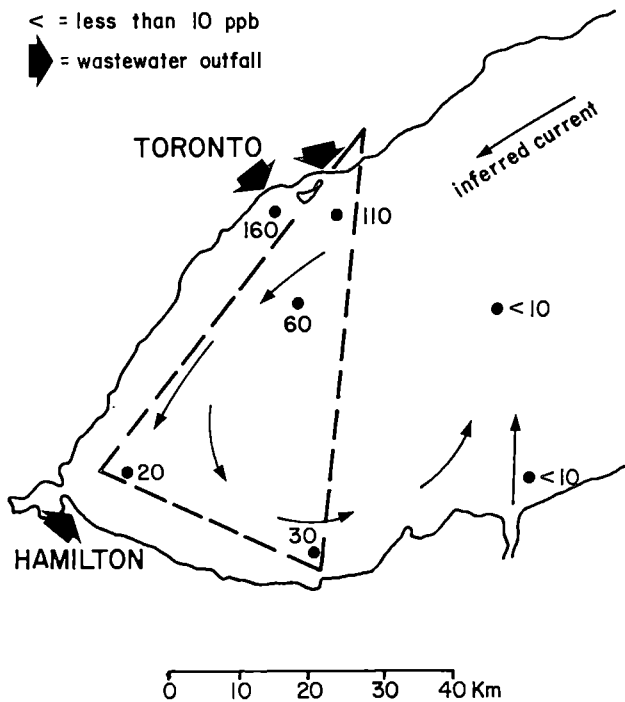


Figure B-1. NTA in western Lake Ontario, January 1972.

The amount of NTA consumed in the Metro area can be estimated from the per capita detergent use and the percentage of NTA in detergents at that time. In 1972, detergents contained about 6% Na_3NTA or 4.5% H_3NTA . For a population of 2×10^6 the annual use of H_3NTA would be about 500,000 kg per year. If the removal of NTA in wastewater treatment was 80% the emission to the lake would be 100,000 kg per year.

The amount of NTA calculated to be present in the 1-m layer is one fourth of this amount, that is, it represents the accumulation of emission of three-month duration with no allowance for degradation in the lake nor for dilution outside the 1-m depth. This does not seem to be an acceptable hypotheses for two reasons: a) the large amount of NTA involved and b) because one month earlier only a small amount was found in the vicinity of Toronto, and in the following month there was not much more than a trace present (20 ppb) and that was at the remote station 8 near Grimsby.

It is noted further that since 1972 the consumption of NTA in the Toronto area (as well as elsewhere) has more than doubled; yet the sampling of the lake in 1975 showed no NTA at or above 10 ppb.

NTA IN WATERWORKS INTAKES ON LAKE ONTARIO

The finished water from ten municipal waterworks on Lake Ontario between Hamilton and Oshawa has been sampled on four occasions (November-December 1972, April 1973, January 1974 and March 1975). In addition to these, 18 other samples have been examined from the Hamilton plant. Of these 54 samples all have had less than detectable levels (10 ppb) except for one sample at Hamilton (June 1974) which contained 20 ppb, and one sample at Oshawa (March 1975) which had 10 ppb.

This stretch of lake shoreline represents the part of the lake most likely to show the presence of NTA from municipal wastewaters. Metro Toronto is by far the largest contributor. The smaller cities are negligible in comparison, and the Hamilton-Burlington outfall is in Hamilton Harbour where further degradation of the NTA in the effluents reduces the output to the lake to a negligible amount.

The anticipated concentration of NTA in lake water can be calculated by assuming that the effluent from Metro Toronto enters a steady littoral current where it is diluted and travels in a confined band along the shore somewhat on the lines of a "coastal jet" (20). The following calculation indicates the maximum concentration which might be expected.

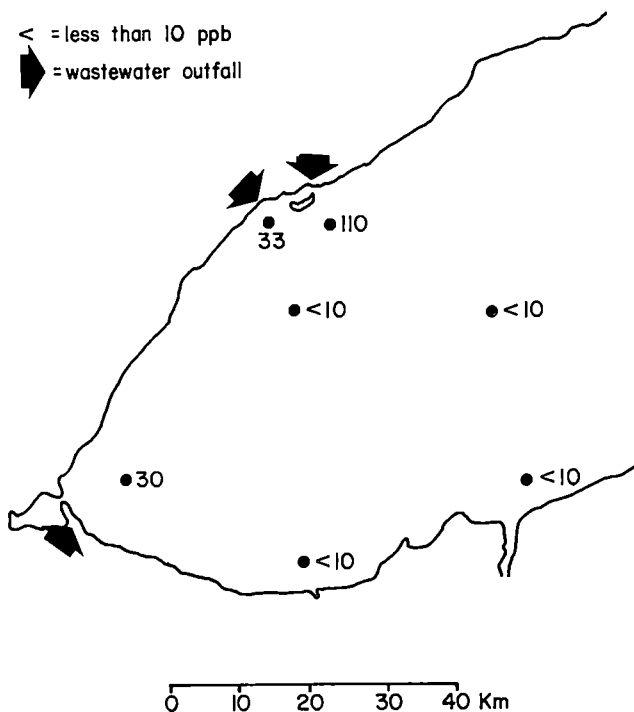


Figure B-2. NTA in western Lake Ontario, July 1972.

Toronto output, based on 1974-1975 detergent consumption and composition and allowing for 80% removal in wastewater treatment, is 250,000 kg H₃NTA per year or 685 kg per day.

If a littoral current is assumed to have a width of 1 km with an average depth of 5 m and an average velocity of 10 km/hr [this is about one half of the average surface current velocity (21)], the volume of water passing Toronto in one day is $120 \times 10^7 \text{ m}^3$. The resulting concentration

is about 0.6 mg/m^3 or ppb.

NTA INPUT TO LAKE ONTARIO BY WAY OF THE NIAGARA RIVER

The mean flow of the Niagara River is 220×10^3 cfs. Assuming a contributing population of one million using detergents at the 1975 rate and composition and making no allowance for NTA degradation in wastewater treatment works, the input of H₃NTA would be 600,000 kg per year and the resulting concentration, 3 ppb.

Montreal Metropolitan Area

This is the only area in the St. Lawrence River system where substantial occurrences of NTA in the drinking water are found, as shown in Table C-1. Figure C-1 is a map of the area with the locations of the sampling points marked. The Ottawa and St. Lawrence rivers come together in Lac des Deux Montagnes and Lac Saint-Louis. As shown in schematic form in Figure C-2, the flow in Rivière des Mille Îles and Rivière-des-Prairies can account for all of the Ottawa River flow, with the St. Lawrence flow going through Lac Saint-Louis. (The flows indicated here were taken from readily available sources and are adequate for the present purpose.)

The NTA concentration in the Ottawa River water entering Lac des Deux Montagnes, based on sample data and concentrations calculated from inputs, is essentially zero. If the contributing population was assumed to be

10⁶ concentrated in the Ottawa-Hull area and if no degradation of NTA occurred in sewage treatment plants or in the river, the river concentration at mean flow would be 23 ppb. Degradation must be taking place, however, reducing the concentration by at least one order of magnitude. Samples taken from the water supplies at Hull, Rockland and Gatineau Mills have all been less than the detectable limit. At Oka, situated at the entrance to Lac des Deux Montagnes, and at two points between the two lakes, six samples contained NTA at less than detectable levels.

Similarly, the concentration in the St. Lawrence flow into Lac Saint-Louis would be expected to be very low, and this is confirmed by samples at Cornwall, Salaberry, Melocheville and the Beauharnois Canal, all of which are below detectable levels.

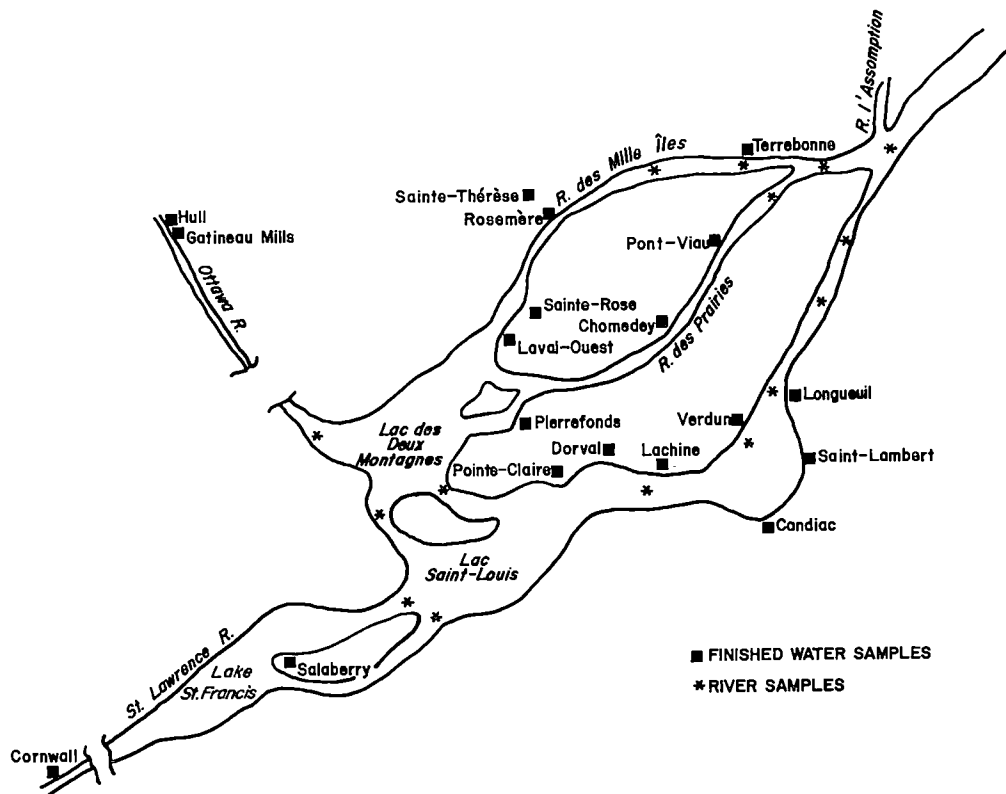


Figure C-1. Map of Montreal metropolitan area indicating sampling points.

Table C-1. Summary of NTA in Finished Water Supplies in the Metro Montreal Area (ppb)

Source	Station	NTA			
		1972	1973	1974	1975
St. Lawrence	Cornwall	<10	<10	<10	<10
Lake St. Francis	Salaberry	<10	<10	<10	
Lac Saint-Louis	Pointe-Claire	<10	20	10	<10
	Dorval	<10	<10	<10	10
	Lachine	<10	<10, <10	10	20
Rivière des Mille Îles	Laval-Ouest	<10	<10	20	-
	Sainte-Rose	<10	<10	20	<10
	Rosemère	<10	<10	30	30
	Sainte-Thérèse	<10	-	20	20
	Terrebonne	<10	<10	20	20
Rivière-des-Prairies	Pierrefonds	<10	<10	<10	10
	Chomedey	<10	<10	<10	<10
	Pont-Viau	<10	<10	20	<10
St. Lawrence	Candiac	<10	<10	<10	<10
	Saint-Lambert	<10	-	-	<10
	Longueuil No. 1	<10	<10	<10	10
	Longueuil No. 2	<10	<10	-	-

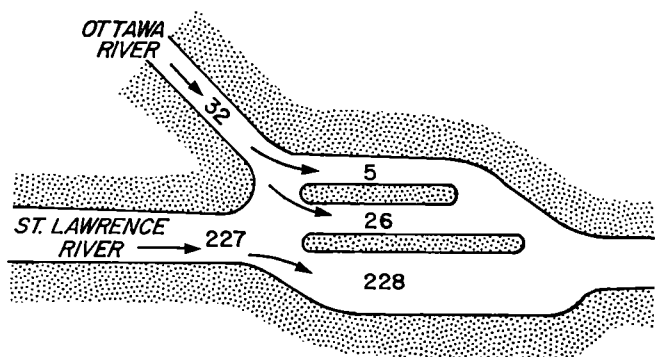


Figure C-2. Flows (cfs x 1,000) in rivers of Montreal area.

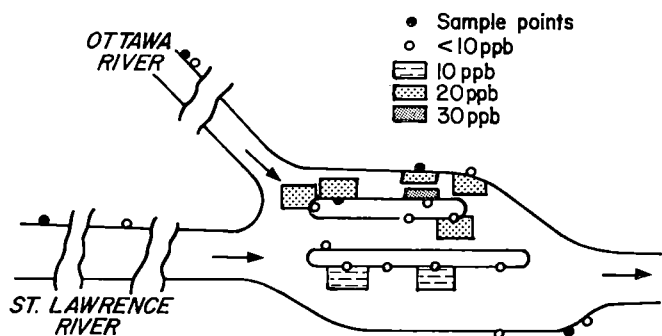


Figure C-3. NTA in Montreal area, 1974.

In the metropolitan area, sampling in 1972 at the points indicated in Figure C-3 showed no values above detection limits. In 1973, one positive value only (20 ppb) was reported for Pointe-Claire, but in 1974 eight samples were at 10 ppb or higher. In Figure C-3, the locations of these are shown with patterns to indicate the concentration. All five samples from Rivière des Mille Îles were positive, at 20 ppb and 30 ppb. In addition, Pont Viau on Rivière-des-Prairies was positive at 20 ppb and two points on the St. Lawrence (Pointe-Claire and Dorval) contained 10 ppb. At the other stations shown on Figure C-3 without patterns, the concentration was below the detection limit.

This distribution of positive values strongly suggests that pollution of the streams is caused by local discharges of sewage. A more complete study of the area would be profitable, but would require information on the position of the waterworks intakes and the location of sewage outfalls, their flows and concentration of NTA in the effluents. From this information it would be possible to calculate the concentrations to be expected after dilution to substantiate the measured values. In the absence of this, it must be concluded that Rivière des Mille Îles receives an amount of wastewater large in relation to its flow and that the smaller concentrations of NTA found at the two stations on the St. Lawrence River result from effluent streams moving downstream along the north shore. It should be noted also that the per capita consumption of NTA in the Metro area at the time of the first sampling was probably less than half that in the time of the 1974 and 1975 sampling.

Table C-2. NTA in River Samples, Entering, within and Leaving Montreal Area (ppb)

Year	Month	River	Station	NTA
1973	May	Ottawa	Oka Ferry	< 10
1973	May		Dorion	< 10
1973	October			< 10
1973	October			< 10
1973	May		Sainte-Anne-de-Bellevue	< 10
1973	October			< 10
1973	May	St. Lawrence	Melocheville	< 10
1973	October			< 10
1973	May		Beauharnois Canal	< 10
1973	October		Lachine Rapids	< 10, < 10, < 10
1973	October		Dock No. 40	< 10, < 10, < 10
1973	May		Concorde Bridge	< 10
1973	October		Lafontaine Tunnel	< 10
1973	June		Varenes	< 10, < 10, < 10
1973	October		Repentigny	10, < 10, < 10
1973	October	Rivière-des-Prairies	No. 11 Bridge	70
1973	May		Repentigny	< 10
1973	October		North Channel at Repentigny	< 10
1973	May		South Channel at Repentigny	30
1973	May	Rivière des Mille Îles	Terrebonne	< 10
1973	October			30
1973	May		Montreal North	10
1973	October			10

Table C-3. NTA in St. Lawrence River, Montreal to the Gulf of St. Lawrence (ppb)

Station number	Station	1973					
		May	June	July	September	October	November
Qu. OB 27	Repentigny					(10, < 10, < 10)	
Qu. OB 1	Lanoraie	< 10	(< 10, < 10, < 10)			(< 10, < 10, < 10)	
Qu. OB 24	Pointe aux Pins	< 10	(< 10, < 10, < 10)			(< 10, < 10, < 10)	
Qu. OB 25	Sorel	< 10	(10, < 10, < 10)			(< 10, < 10, < 10)	
Qu. OD 30	Cap-de-la-Madeleine						
	North shore		(< 10, < 10, < 10)			(< 10, < 10, < 10)	
Qu. OD 31	Trois-Rivières						
	South shore		(< 10, < 10, < 10)			(< 10, < 10, < 10)	
Qu. PC 1	Portneuf		(< 10, < 10, < 10)			(< 10, < 10, < 10)	
Qu. PE 1	Quebec City					(< 10, < 10, < 10)	
Qu. PH 1	Lévis		(< 10, < 10, < 10)				
Qu. PJ 12	Sainte-Foy				(< 10, < 10, < 10)		
Qu. PK 6	Cap à la Roche						(< 10, < 10, 10)
Qu. PL 8	Pointe-Lottinville					(-, < 10, < 10)	

Note: Three amounts in parentheses indicate three samples taken at ten-minute intervals.

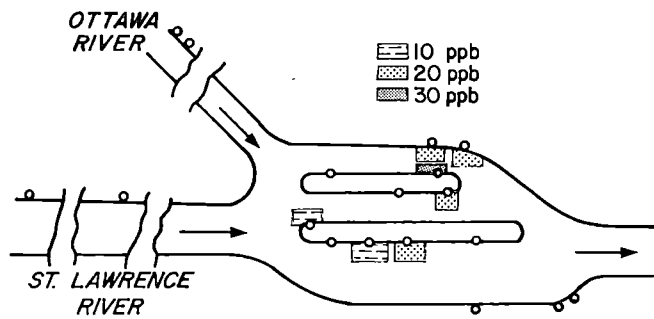


Figure C-4. NTA in Montreal area, 1975.

The 1975 sampling in the Metro area shows substantially the same situation. Seven samples (instead of eight) were positive but one sample point, previously positive, was not received. Figure C-4 shows the location of samples

containing NTA at levels of 10 ppb or more.

River sampling which was done in 1973 (Table C-2) confirms this explanation of the occurrences of NTA in the area. In the St. Lawrence River section from the Lachine Rapids to Varennes, five stations all had samples at less than detectable levels. At Repentigny, below the confluence of the three rivers, one sample contained 10 ppb and two were below the detection level.

MONTREAL TO THE GULF OF ST. LAWRENCE

This stretch of the St. Lawrence has no large inputs before Quebec City. At the head of Lac Saint-Pierre, the Richelieu River enters the lake as well but is also very low in NTA. The effect of wastewater discharge from Quebec City into the large flow of the river is not great enough to be seen. The data are summarized in Table C-3.

Photochemical Degradation of NTA

Appendix D is an estimation of the rate of the photochemical degradation of NTA in open waters, prepared by Dr. John Carey, Water Chemistry Section, CCIW.

According to the *Kirk-Othmer Encyclopedia of Chemical Technology*, during mid-day on a typical clear midsummer day in Cleveland, Ohio, 1,198 $\mu\text{W}/\text{cm}^2$ of energy between 3,000 Å and 3,700 Å are available. If eight hours of light are assumed at this value, the total energy per clear day will be:

$$28,800 \times 1,198 = 34.5 \text{ J}/\text{cm}^2/\text{day}$$

If the average wavelength is 3,500 Å (i.e., 28,571 cm^{-1} / quantum or 341,709 J/einstein), then the total light available is:

$$1.01 \times 10^{-4} \text{ einsteins}/\text{cm}^2/\text{day}$$

If 90% of the light is lost to scattering and of the remaining light, 99% is assumed to be absorbed by species other than FeNTA, then the light absorbed by FeNTA is:

$$1.01 \times 10^{-7} \text{ einsteins}/\text{cm}^2/\text{day}$$

If the quantum yield for FeNTA reaction is 0.05 (based on NTA), then this will result in degradation of:

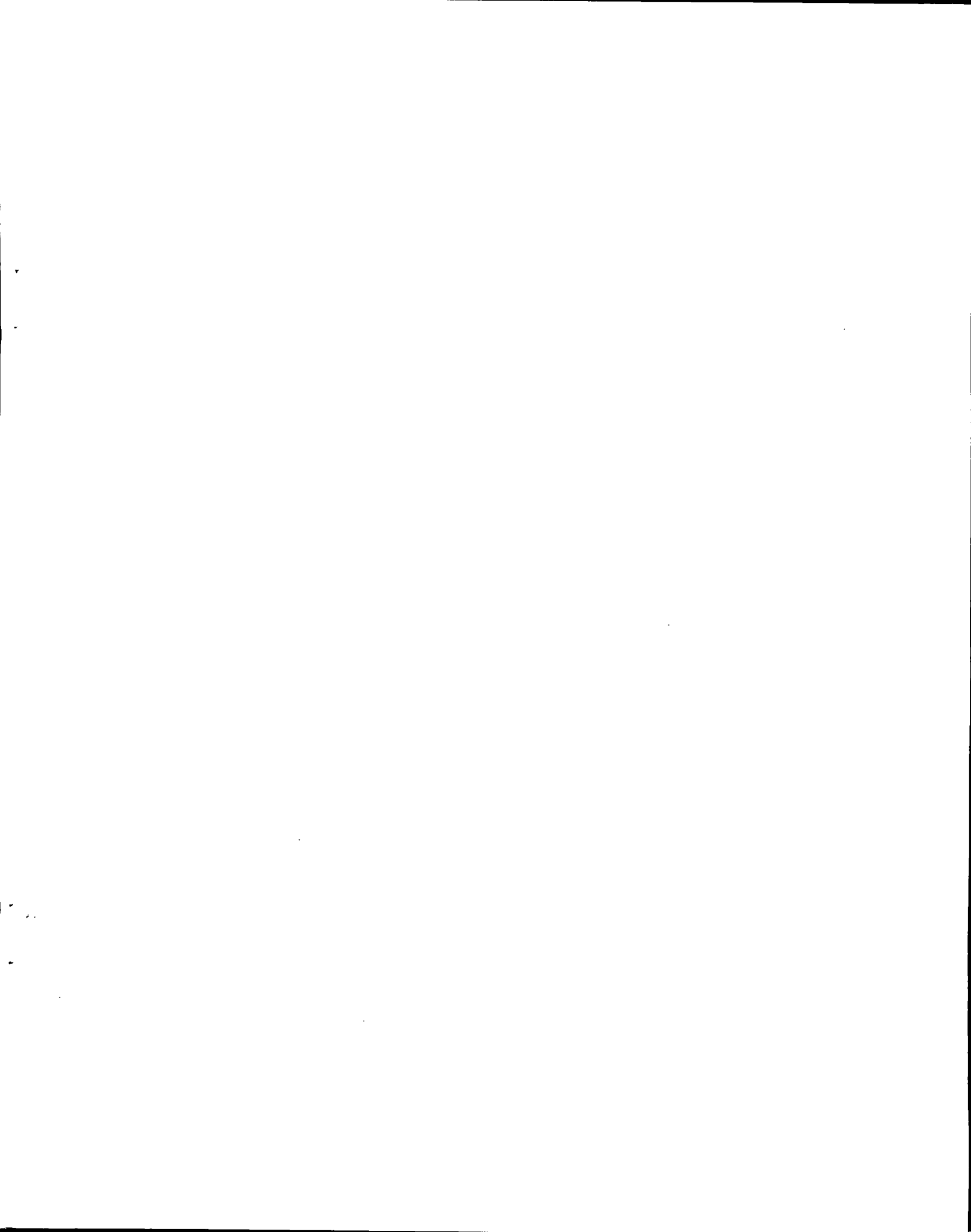
$$5 \times 10^{-9} \text{ mol}/\text{cm}^2/\text{day}$$

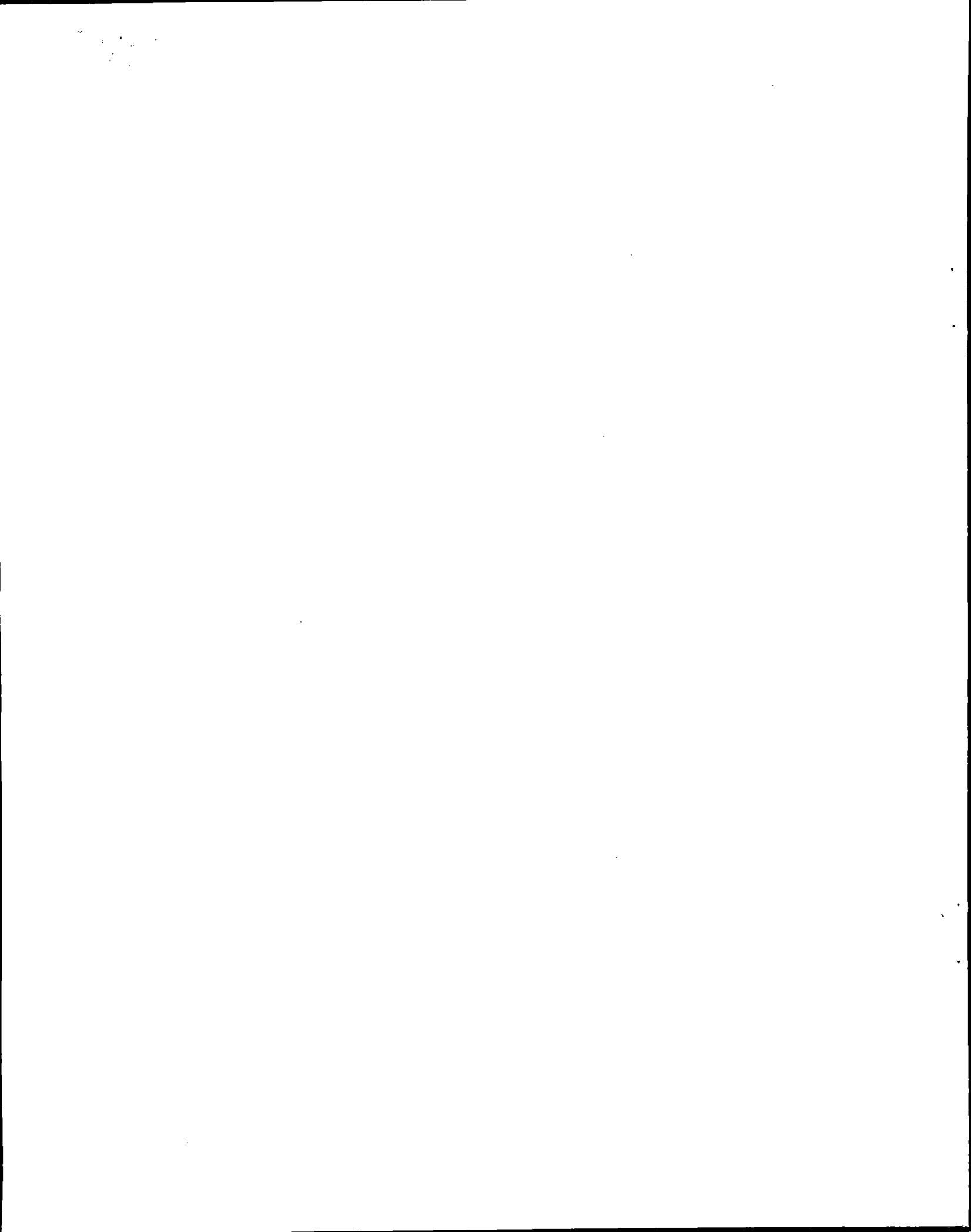
If the total NTA concentration is 20 ppb, i.e., $1 \times 10^{-7} \text{ M}$, and all of this is assumed to be in the form of the iron (or copper complex), then NTA degraded would represent all the NTA to a depth of 50 cm.

This calculation, however, assumes that the reactive NTA species absorbs 0.1% of the available light. If the average extinction coefficient over the above wavelength range is 500 and the NTA concentration is 20 ppb, total absorbance would not be reached until there was a pathlength of

$$\frac{2}{500} \times 10^7 = 4,000 \text{ cm}$$

Thus if light could penetrate a depth of 40 m, and if the concentration of ferric or copper NTA was enough to absorb 1% of the light that was not scattered, and if 90% is realistic for the amount of light lost to scatter, then the NTA species would decompose by 1.25% per eight hours of sunlight, or a half-life of about two months.





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