POLLUTION CONTROL AT A LARGE FERTILIZER COMPLEX

Although this fertilizer complex was originally designed to meet pollution control requirements, inadequate waste treatment, operating rates over design, and revisions of government regulations required additional pollution abatement procedures.

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One of the major developments in the industrial world has been the recent construction and operation of multi-plant fertilizer manufacturing complexes. The heart of these complexes is usually a large single train ammonia plant. Integrated with it are various combinations of plants for the production of nitric acid, ammonium nitrate, phosphoric acid, ammonium phosphates and urea. This concentration of large scale facilities and the improved processes which have been incorporated into the operations have enabled considerable economies in production costs. It has also provided a potential for the release of greater quantities of pollutants, and has required increased care to control the emissions and protect the environment.

Canadian Industries Limited operates one such fertilizer complex at its Lambton Works site, which fronts on the St. Clair River about 15 mi. south of Sarnia, Ontario. Construction began in 1965 and the Works has been in production since the fall of 1966. The land in the area is very flat and basically rural in nature. In 1965 the only other industry in the immediate neighborhood was a large coal burning generating station located in the U.S. on the other side of the St. Clair directly across from the CIL site. The main section of the well known Sarnia "Chemical Valley" began some 9 mi. north of the site. Since that time several small plants have been constructed closer to the Works and a 2,000 mw coal burning power generating station has been constructed about 2 mi. north on the Canadian side of the river.

The various plants in the CIL complex were designed by their contractors to meet the existing Ontario air and water quality requirements. There were no regulations for soil pollution or for solid waste disposal. In general, the treatment systems provided have functioned satisfactorily. However, a number of pollution control problems have arisen due to several factors, including inadequate treatment, operating rates over design, and revisions of government regulations.

Although pollution abatement facilities were expected to enable air quality regulations to be met, CIL decided that it would be desirable to monitor its operations to ensure that this was being accomplsihed, to indicate the malfunction of pollution control equipment, and to enable repair of such equipment before environmental damage could occur. An air quality survey therefore, was begun in July 1965, approximately one year prior to the scheduled start-up of the fertilizer complex, so that a history could be obtained under this regime for comparison purposes at a later date. The three potential contaminants considered necessary for an adequate survey were fluorides, sulfur dioxide, and particulate matter. Fluorides would normally be released during operations of the phosphoric acid-diammonium phosphate plants, while sulfur dioxide would be produced thorugh the combustion of fuel by both CIL and the generating station. Particulate matter would originate in CIL operations and form a number of other sources such as the generating station and local farming.

The survey sampling grid was set up by drawing circles on a map around the center of the plant with radii of ½-, 1-, 2-, and 3 mi. From the center, lines were drawn in the eight cardinal directions, their intersections with the circles being the desired locations for the sampling stations. The actual locations were chosen by modifying the above where necessary for reasons of accessibility and protection from vandalism. In addition to these locations, a number of others were selected to help round out the survey. The grid was initially composed of 35 stations and underwent several expansions to a total of 42. Average monthly ground level flouride and sulfur dioxide concentrations and dust deposition rates were measured at each station by means of lime candles, lead peroxide candles, and dustfall cans respectively. The results were marked on individual area maps from which monthly isopleths were drawn. Sampling of timothy forage at a number of stations and analyses for fluoride content were also carried out during the growing season.

Comparison of the sulfur dioxide and dust deposition rate isopleths before and after Lambton Works start-up showed that they had not been significantly affected by operations at the fertilizer complex. The fluoride concentrations, however, have been significantly increased by plant emissions, as was revealed in the isopleths.

Even prior to start-up the ground level fluoride concentrations at a number of stations had been relatively high, at times exceeding values where damage could be caused to cattle if extended ingestion of contaminated forage occured. Presence of these high values provoked questions as to their origin. A graph was prepared, Figure 1 which showed the average concentrations of fluorides and sulfur dioxide for all stations on the grid for each month before start-up. Since the only large source of sulfur dioxide at the time was the power generating station across the river, an examination of the close parallel between the lines for the two contaminants leaves no doubt as to their common origin in the combustion of coal.

Fluoride emissions

Fluoride emissions, which are various mixtures of hydrogen fluoride, silicon tetrafluoride, and fluosilicic acid, originate in several areas of the fertilizer plant operations. Wet process phosphoric acid is produced by reacting sulfuric acid with fluorapatite [$Ca_{10}(PO_4)_6F_2$] or phosphate rock. By-product calcium sulfate is formed and filtered off and the phosphoric acid is concentrated in evaporators to about 54% P_2O_5.

Some fluorides are driven off with the evaporated vapor, and this stream is scrubbed to remove fluosilicic acid for sale. The vapor and unabsorbed fluorides are consensed in a barometric condenser, with the liquid effluent flowing to gypsum ponds, which are large dyked areas. Miscellaneous fluoride emissions from the acid production process are passed through another scrubber with the absorbed material also flowing to these ponds, and the unabsorbed portion being released to atmosphere. Emission rate of the latter is almost negligible. The filtered calcium sulfate is slurried in gypsum pond water and transported along with dissolved fluorides to the ponds where the sulfate settles out and the clear liquor is cooled for reuse in the process. The high fluoride concentrations and low pH of the liquor due to the presence of acids tend to cause fluorides to be evolved from the ponds into the atmosphere.

The major source of fluoride emission to the atmosphere is the diammonium phosphate plant (DAP), where phosphoric acid is reacted with ammonia. Most of the fluoride present in the acid is released at this site, the majority evolved in the reactor with minor amounts evolved in the granulator, dryer, and cooler. Gaseous effluent from the reactor and granulator are combined and passed through a cyclonic spray "ammonia scrubber". In the original installation the gas from this unit was then discharged up the "ammonia scrubber" stack. Gases from the dryer and cooler are also combined, passed through a cyclonic spray "dust scrubber" and discharged up the "dust scrubber" stack.

Where before fertilizer plant start-up there was only one source emitting fluorides there now were several and, therefore, concentrations at the sampling stations had increased. Because of experience being gained elsewhere in fluoride induced damage the Ontario Department of Health became concerned about this increase about one year after the fertilizer complex began operating. They requested that CIL participate in a program to reduce the emission of fluoride bearing materials so that the isopleth for 100 mg. F/100 sq. cm./30 days was restricted to plant property. According to the Department of Health, world opinion at the time suggested that if concentrations were kept below this value, as measured by candle techniques, cattle damage from eating contaminated forage was unlikely to occur. CIL agreed to the request even though the area was negligible. This was later confirmed in a vegetation survey carried out by an independent research institute.

Ground level concentration data

The problem became a determination of the most effective and economic way of meeting the objective of the Department of Health, taking into account the fluorides emitted by the generating station, over which CIL had no control. Three sets of ground level concentration data were available to assist in this determination.

1. Data before the fertilizer plant start-up when the only emitter was the power generating station.
2. Data obtained when this station, the DAP plant and the gypsum ponds were all operating.
3. Data obtained during a maintenance shutdown of two weeks duration when only the station and the gypsum ponds were operating.

Periods were fortunately available when weather and most other conditions were essentially similar for all cases. By simple addition and subtraction, therefore, a set of data was obtained which roughly could be attributed to the effect at each sampling station from each source. It was decided to fit empirical equations to this information by the method of least squares. For each basic source-generating station, DAP plant and gypsum ponds-dispersion equations of the following general form were obtained:

$$Co = \frac{K}{r^n} exp(-A - \frac{B}{r}) \quad (1)$$

where Co is the ground level concentration at a point.

r is the distance from source to the point.

K,n are constants.

A,B are values dependent on the direction from source. A good fit could be made if they were represented by the truncated Fourier Series:

$$A = \sum_{k=1}^{3} [D_k \cos(k\theta) + E_k \sin(k\theta)] \quad (2)$$

$$B = \sum_{k=1}^{3} [F_k \cos(k\theta) + G_k \sin(k\theta)] \quad (3)$$

where θ is the angle measured from north through source.

$D, E, F, G,$ are constants.

With the resulting model it was thus possible to simulate any combination of circumstances by mathematical means. Account could be taken of change of direction of the prevailing wind during the month, the change in vapor pressure of fluoride in the gypsum pond water, and variations in DAP plant output. Figure 2 shows the computed and measured 100 mg. isopleth for November 1968. At that time the plant emissions were 62% of those during the test period, the prevailing wind direction had veered 90% from standard and the temperature had dropped so that fluoride vapor pressure was about 25% of the standard during the test period. After studying many hypothetical cases it was concluded that the optimum procedure for meeting the Ontario Government objective was to reduce fluorides emitted from the DAP plant from approximately 300 lb./day to a total of about 50 lb./day, and to purchase some land south of the gypsum ponds to extend the company owned buffer zone around the plant. Use of such zones is common in the phosphate industry.

Shortly after this study was completed the Ontario authorities changed their air quality objective. Instead of a measured monthly average ground level concentration of 100 mg./100 sq. cm./30 days, new regulations called for a maximum calculated average ground level concentration of 10 ppb fluorides outside company property based on the Pasquill-Gifford dispersion formula, the Holland plume rise formula, and a 30 min. period. These equations are commonly used with stacks but their appplication to area emissions, such as from gypsum ponds, is not as well developed.

With their use it was found that the new objective could be met at the DAP plant with a maximum emission of 160 lb./day. This would best be done by reducing fluoride emissions from the ammonia scrubbing system, combining this effluent with that from the dust scrubbing system, and discharging the mixture into the dust scrubber stack. The emission of 50 lb./day previously mentioned should not be directly compared with the 160 lb./day because of the different basis of the standards. In addition, in the latter case the two effluents from the plant were combined and discharged up the higher stack and there was no necessity for taking the emission from the generating station into account.

Tests had suggested that most of the fluoride leaving the ammonia scrubber was present as a mist of a size greater than 3 m. After some study, therfore, it was decided to reduce the emission by installing a venturi scrubber between the ammonia scrubber and the dust scrubber stack, using gypsum pond water as the scrubbing medium. It was estimated that total emissions from the DAP plant would thereby actually be lowered to 50- 80 lb./day, equivalent to a calculated 5 ppb F maximum. This was fortunate because shortly thereafter the Ontario standard for fluorides was lowered from 10- to 5 ppb. The venturi scrubber has recently been installed and preliminary tests indicate that it is doing better than originally estimated; in fact the new standard is being exceeded more than met. The question of how releases from the gypsum ponds will be treated under the new regulation remains to be settled. It would appear that purchase of the additional land to extend the buffer zone will be satisfactory as long as negligible fluoride induced damage can be detected outside plant property. This land has accordingly been purchased.

Particulate emissons

The most recent change in Ontario air quality regulations for fluorides was accompanied by one for suspended particulate matter: the maximum average calculated ground level concentration for all areas became 100 mg. cu. m. At Lambton Works some solids are emitted from the urea and ammonium nitrate prill towers. Based on very preliminary estimates, provincial authorities believed the combined discharge from these towers produced a calculated maximum concentration exceeding regulations. CIL was requested to carry out a study to more accurately define the situation and to be prepared to take corrective measures if transgressions were occurring. The major parameters to be determined in the study were total weight discharged, size breakdown in percentage by weight, and volume flow. Size breakdown was necessary because the Pasquill-Gifford equation only applies to matter below a certain size, which for Ontario regulations is taken as 44 m.

The design and operation of prill towers is such that determination of the major parameters listed about poses considerable difficulty. Nevertheless, reliable values were obtained which proved that, in fact, the legal standard was not being exceeded outside company property. However, some ammonium nitrate and urea still fall within the site itself, and are a potential source of water pollution through storm water runoff. The problem is common to most plants of this type and Lambton Works would appreciate exchanges of information on how it should best be controlled.

There are a number of other potential pollutants at Lambton Works including oxides of nitrogen in the tail gas from the nitric acid plant, and ammonia. To date, however, these have presented no real problem.

Water quality monitoring

It was decided to proceed with a monitoring program on the effects of liquid discharges from the Works for the same reasons indicated for the air monitoring program. No matter how carefully the pollution control facilities are designed or operated, there is a chance that there may be some unpredicted effect or that some leak of pollutants will develop. In order to protect themselves, therefore, CIL and some other chemical companies are undertaking biological surveys in receiving waters which cover periods before and after plant start-ups.

The Lambton Works effluent stream discharges into the St. Clair River, where there is already considerable pollution. To complicate the development of a system to monitor this effluent, the existing pollution in the river was of a random nature indicating that there were intermittent discharges or spills of pollutants from the industries located upstream. Mathematically the problem was to find a statistical method which would enable the company to separate the effects of its effluent from the random effects of other upstream effluents.

In March 1965, six sampling stations were selected along the St. Clair River. One of these was a control point chosen with the expectation that it would be as free as possible from the pollution generated along both sides of the river. The other five ranged down the Canadian shore, one above the four below the future CIL plant outfall. The distances from shore ranged from 50- to 100 ft., with each sampling point covering an area roughly 10- by 10 ft. Depth of water varied from 5- to 20-ft. In each survey samples of the river bottom were taken and sieved through a 30 mesh screen to retain all animals of the macroinvertebrate fauna. These consisted almost entirely of chironomidae (midge larvae), pelecypoda (bivalves), gastropoda (snails), and oligochaeta (worms). The samples were preserved and taken back to a consulting biologist's laboratory where they were sorted into the groups listed above and counted. The original control point was soon relocated because of too much pollution. One of the original sampling stations was also relocated and one discontinued because of the difficulty in getting representative samples. The final station selections were set by November 1965, approximately one year before scheduled plant start-up. From then on surveys were carried out at roughly three to four month intervals.

In studying the data accumulated from several sampling periods prior to the start-up it was noted that the population of a particular group of animals at different stations seemed to follow the same fluctuations with time. The hypothesis, therefore, was mathematically tested that the population of this group at one station was directly proportional to the population at another station, and that the constant of proportionality was independent of time. Results of the tests confirmed the hypothesis. The difference between the animal counts at any two stations could, therefore, be used as an indicator of pollution entering the river between the two stations. Presence of additional pollution at the downstream location would cause the difference to increase which could be recorded.

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As is often the case with biological populations of this type, it was observed that the variability in numbers of animals found from sample to sample at any given location tended to be proportional to the density of animals at this particular location. To permit using the standard analysis of variance technique it was decided, therefore, to stabilize the variance by applying the logarithmic transformation re commended in such cases.

Control charts similar to the well known quality control charts were prepared using the data obtained before start-up, and those which proved most useful for monitoring purposes were determined. The data obtained after start-up could be measured against standards by plotting on these selected charts.

When a point on the charts is inside the 95% control limits the situation is considered normal, and no pollution by Lambton Works has occurred. When several consecutive points taken at normal time intervals fall between the 95- and 99% limits, a survey should be carried out as soon as feasible to check the findings. If the new point should still be between the limits action should be taken inside the works to find the cause of the pollution. When a point falls outside the 99% limits the situation is also considered abnormal, and if no immediate reason is at hand the same action described above should be taken. Even though the points all lie within the 95% limit, over long periods of time there should be a scatter about the center line. If not, the situation would also be considered abnormal but not serious.

These charts have been in use since plant start-up and, for example, showed the effect of an inadvertent discharge of ammonia to the river. This illustrated in Figure 3 where the control chart for pelecypoda compares conditions at stations 1A and 2 which are, respectively, just upstream and downstream of the outfall. Of the groups found in this survey it was expected that pelecypoda would be most readily affected by impurities in the water, since they are filter-feeders.

The solid circles represent data obtained prior to start-up of Lambton Works, the hollow circles data subsequent to that time. It will be seen that conditions were outside the 99% control limit at the first survey after start-up. This was due to a scouring out of the river bottom observed at the time of sampling. On the next sampling the value for pelecypoda was still outside the 99% limit but was moving towards it. During the last day of June 1967 and the first few days of July operating difficulties at the ammonia plant resulted in the inadvertent discharge of ammonia. The result of the first survey after the discharge showed that the value for pelecypoda had moved further away from the 99 per cent control limit.

The discharge of ammonia had affected the pelecypoda, and also the oligochaeta, at station 2 just below the outfall and this had been revealed in the control charts. The conditions at stations further downstream had not been affected, however.

The method of basing control charts on the **differences** in the number of animals found at stations upstream and downstream from the outfall being monitored permits one to detect a significant change caused by material discharged through that outfall in spite of very large fluctuations in the number of animals caused by random discharge of pollution material released upstream.

To complement this biological survey in the waters receiving the Work's effluent, chemical monitoring of the effluent itself was also carried out once plant operations began.

Ammonia plant condensate

A condensate stream containing about 800 ppm ammonia and 2,000 ppm carbon dioxide is generated in the ammonia plant at the rate of about 200 gal./min. Provincial authorities would not allow discharge of this stream to the river because of its ammonia content, even though it would be mixed with the main plant effluent of about 62,000 gal./min. When the ammonia plant began operating there was no other means on hand for disposal and it was directed to one of the gypsum ponds, which was empty, as an expediency. This procedure could not be long continued, however, as the pond eventually began to approach the overflow mark. An extensive study was carried out to determine the optimum means of handling the stream which culminated in a recommendation that it be pumped down disposal wells. Two wells were subsequently drilled and successfully used for 18 months.

Unfortunately, there are a number of abandoned exploratory oil wells in the area, and recently two of them began to slowly leak ammoniacal brine to the surface. Under normal conditions it would take many years for the condensate stream to reach the abandoned wells and the rapid development of ammoniacal leaks is apparently due to underground fissures. Use of the disposal wells was stopped at the request of the government and the condensate stream once again directed to the gypsum ponds to avoid shutting down the ammonia plant. A review of the situation indicated that the oil wells had been plugged to standards considered acceptable at the time. In order to allow for at least temporary reuse of the disposal wells it was decided to replug the oil wells to the more reliable present day standards. This relatively expensive procedure has eliminated the leakage. There are a number of other abandoned wells in the area, however, and it was realized that they too might begin to leak at some future date, unless the disposal wells were closed down. The study of other methods for treating the ammonia condensate stream was begun once more, and results to date indicate that ammonia stripping or ion exchange, or a combination of both may be suitable. In the meantime, discharge of the condenstate stream to the gypsum ponds has been discontinued. A portion of the flow is presently being disposed of to the wells while the remainder is being handled in several experimental programs.

Although the initial plant effluent facilities and layout were accepted by the Ontario Water Resources Commission there was almost no equipment for trapping spills or preventing objectionable chemicals from entering drainage ditches and, thereby, the St. Clair River.

It was noted soon after beginning operations that excessive quantities of ammonium compounds, phosphates and fluorides were being found in the effluent stream. Ontario authorities requested that these quantities be reduced, particularly the first two which are nutrients.

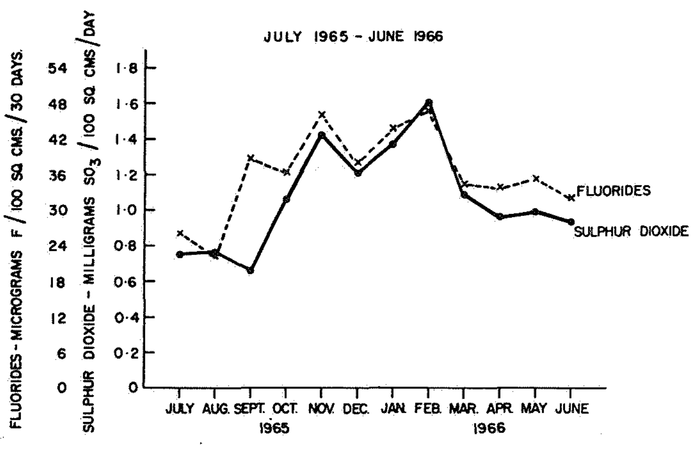


Figure 1. Average monthly concentrations of fluorides and sulfur dioxide for all grid stations before plant start-up.

Some of the ammonia and the nitrate in the effluent arises from non-steady state occurrences, such as leaks, spills, and process upsets. A number of steps have been taken to prevent the escape of these materials, such as the installation of tanks to retain liquor in the event of upsets and the installation of a composite sampler and automatic analyzers for ammonia and nitrate ions on the main effluent stream. These instruments can indicate the presence of unacceptable levels of ions but cannot locate their source. A project is now underway to install a number of pH and conductivity instruments at various locations throughout the works. This will enable the quick pinpointing of a leak or spill, and allow corrective action to be taken before damage can occur.

The presence of free ammonia, which can occur in an alkaline solution, is very toxic to fish life. A system has been provided for rapid acidification of the main effluent with sulfuric acid in the event of excessive quantities of ammonia being found. This presently eliminates the necessity of constructing a retaining basin for the stream, which would be both large and expensive.

Discharge of phosphates and fluorides to the St. Clair River was virtually eliminated by the construction of a small dam on the main ditch in the area. All liquids trapped by the dam are recycled to the gypsum pond.

Solid waste disposal

Solid waste disposal, which by definition includes liquid wastes which cannot be treated for discharge in the liquid effluent, has rapidly grown to equal importance with water and air pollution as a universal problem.

Among these wastes at Lambton Works are sulfinol reclaimer bottoms from the ammonia plant, used oil from

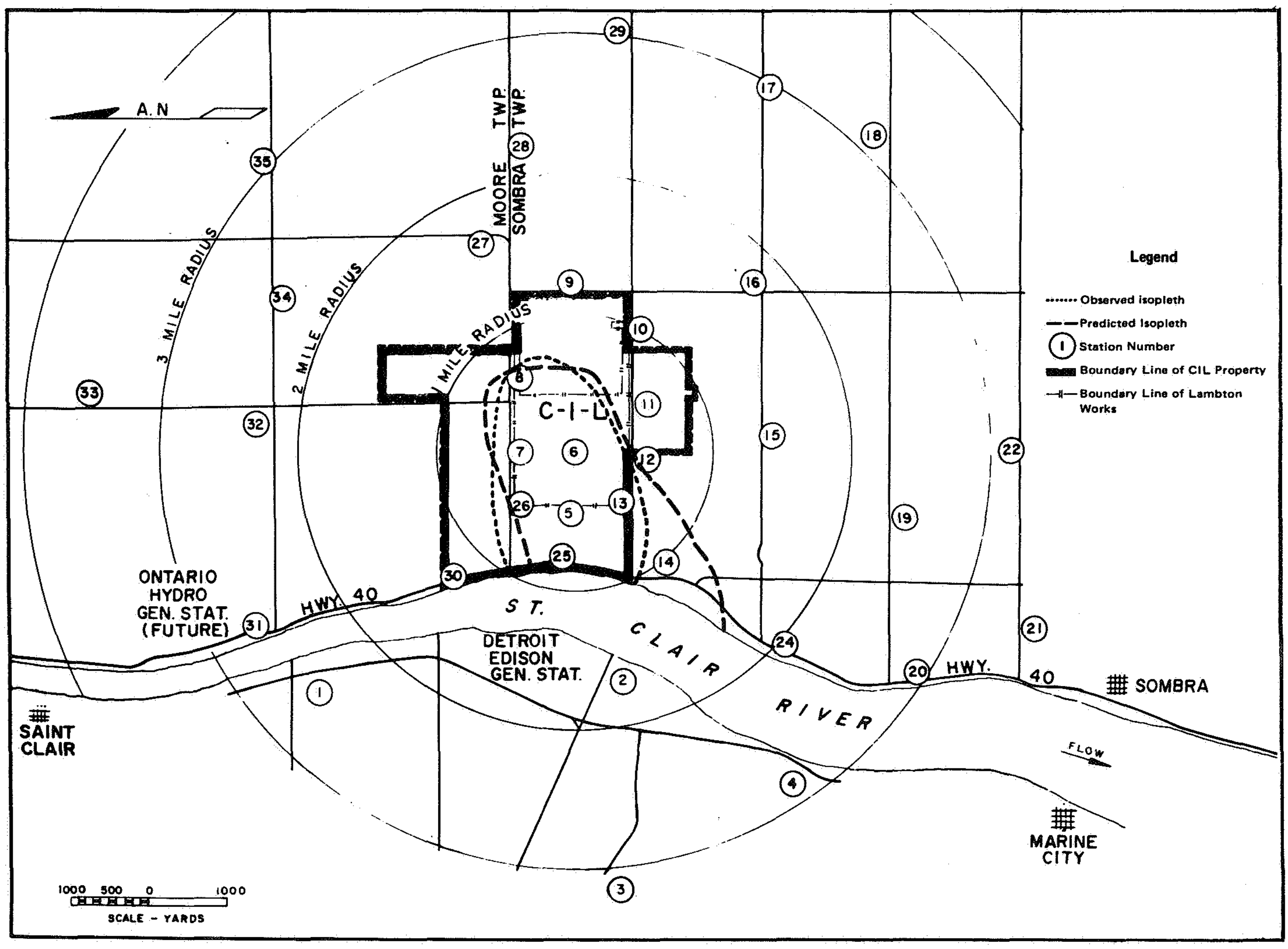


Figure 2. Computed and measured 100 mg. isopleth for November 1968.

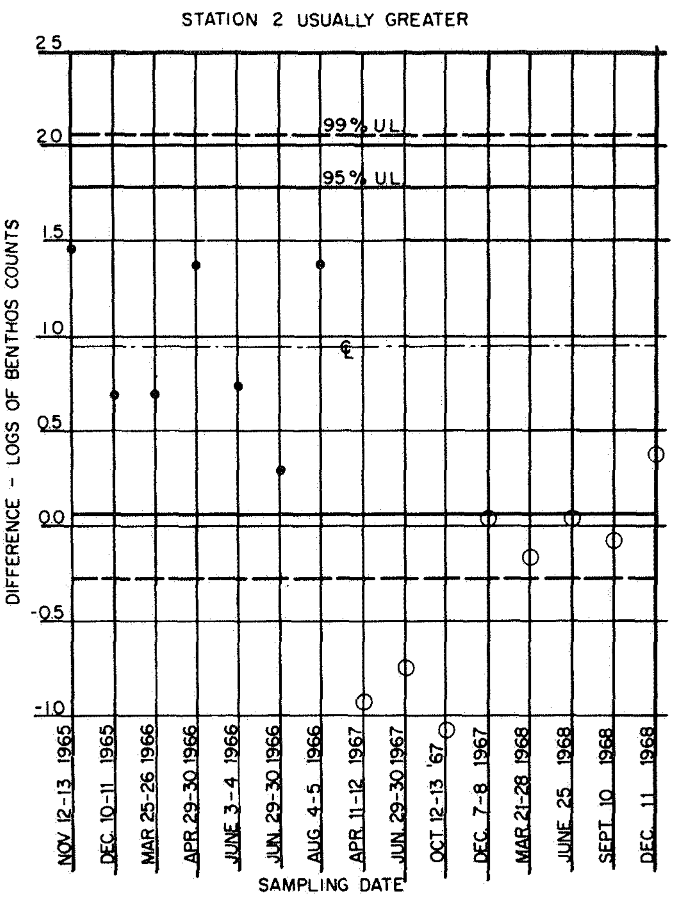
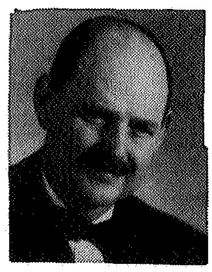


Figure 3. Pollution control chart for pelecypoda compOaring conditions upstream and downstream of the outfall.

compressors, pumps, etc., phosphoric acid plant scale, DAP plant scale, warehouse waste, etc. An independent contractor operates a disposal service in the area to handle wastes from many plants in the "Chemical Valley". His service includes several incinerators, a disposal well and dumping grounds. Lambton Works waste is collected by this contractor, some of it for incineration and some for direct burial. In this manner a potentially troublesome problem has been avoided.

Noise is increasingly being considered as another form of pollution. The principle sources of noise at Lambton Works are steam and other gases vented during the start-up and shutdown of the ammonia plant. A silencer was originally provided for the main vent for waste gases. Additional silencers have been, or soon will be installed on the high and low pressure steam vents and the surface condenser auxiliary vacuum ejector.



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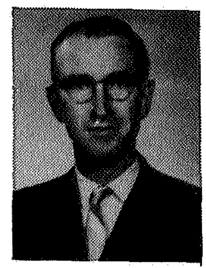

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