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SOURCES OF NITROGEN AS A WATER POLLUTANT INDUSTRIAL WASTE WATER

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The paper discusses the very few estimates of industrial nitrogen discharges presented in the literature. For some industrial branches new estimates are given, based on detailed measurements. The paper ends up in an actual estimate of the total industrial contribution of nitrogen to Swedish surface waters of about 10,000 tons/yr, representing 8 % of the total nitrogen transport to surface waters in the country.

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SOURCES OF NITROGEN AS A WATER POLLUTANT: INDUSTRIAL WASTE WATER.

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Comparatively few good estimates as to the relative importance of different sources of nitrogen transport to surface waters from large areas, such as whole countries, can be found in the literature.

One early study with the aim of covering the whole territory of the United States was carried out by an American Water Works Association Task Group in 1967. The figure they arrived at concerning the annual quantity of nitrogen reaching the surface waters of the USA, ∿ 2.5 million tons, might merely be regarded as a qualified guess than a scientifically based estimate. The industrial share of this amount would be in the order of 20 %. In this context, as well as in the following, the concept "industrial sources for nitrogen" is understood as the nitrogen waste discharged directly from industrial installations. Consequently, industrially produced nitrogen compounds, spread in the environment for certain purposes, such as fertilizers, are not included.

Relative importance of various sources

A more detailed survey of the magnitude of the nitrogen contributions from various sources to the surface waters of the State of California, was carried out by Jenkins et al (1973).

They arrived at an estimate of the total annual nitrogen transport to surface waters of the state of about 260,000 tons. The industrial share of this sum was estimated at about 50,000 tons, constituting approximately 20 %. The amount of nitrogen discharged with the industrial waste water corresponded rather well to the estimate of nitrogen in sewered municipal waste in California, 51,500 tons/yr.

Vollenweider (1968), when discussing the estimated export of nitrogen in the total run-off from a representative area with a population density of 150 inhabitants/km^2 and including both municipal and industrial wastes, comes to an industrial contribution of less than 10 % of the total amount from point sources (0.80 g N/m^2, year). However, this probably is an underestimate if the average for a whole country is considered.

In Finland, an estimate for 1972 shows that the annual nitrogen discharge from the industry, 9,200 tons, might be approximately the same as the total municipal discharge (Särkkä, 1974). The quite dominating part of the industrial nitrogen losses in Finland comes from the pulp and paper industry (∿60 %). It therefore must be born in mind that the estimates of the mean specific nitrogen discharges from the different types of pulp industry, used as a base for the calculations of total discharges, are very uncertain. Furthermore, the specific nitrogen discharges given by Särkkä (1974) are in several cases higher than those found by other workers (see below). In conclusion, the figure given for the nitrogen losses from industrial sources to surface waters in Finland, might be a slight overestimation.

For Sweden, a rough estimate of the industrial contribution to the nitrogen transport to surface waters has been given by Ahl and Odén (1974), who propose the figure 30,000 tons/yr. This quantity amounts to 150 % of the municipal contribution, thereby being the highest relative whole-country-estimate for the industry presented so far. However, the authors state that the figure for the industry is uncertain, due to lacking statistics and due to the rapid development concerning the treatment of industrial waste waters.

A more recent estimate, based on a much more solid background material was given by Hansson (1975), who came to a total industrial nitrogen discharge in Sweden of 8 - 9,000 tons/yr, being approximately 50 % of the municipal nitrogen discharges. However, in this sum, the contribution from the forest industries (1,650 tons/yr) probably is underestimated (see below). Calculations of the amounts of nutrients transported to Lake Vänern and Lake Mälaren, respectively, have also been carried out.

The totally 12,820 tons of nitrogen being annually transported to Lake Vänern can be divided on different sources according to table 1 (SNV, 1972:6).

TABLE 1

Sources of Nitrogen Transport to Lake Vänern

Source	Fraction of N-transport (%)
Agricultural drainage	54
Forest drainage	23
Municipal wastes	6
Forest industry	5
Chemical industry	10
Other industries	2
Total	100

The industrial sources, thus, would contribute to the nitrogen input to Lake Vänern by about 2,200 tons/yr.

The different nitrogen sources to Lake Mälaren have relative importances as shown in table 2 (Ahl, 1973).

TABLE 2

Sources of Nitrogen Transport to Lake Mälaren

Source	Fraction of N-transport (%)
"Natural"	26
Municipal	16
Industrial	20
Agricultural	38
Total	100

Industrial nitrogen sources

The relative importance of different industrial branches to the total discharge of nitrogen from industrial sources has been quite differently estimated in Finland and Sweden. The estimates for Finland in 1972 given by Särkkä (1974) are shown in table 3 together with the estimates for Sweden, presented by Hansson (1975).

TABLE 3
Estimates of Annual Industrial Nitrogen Discharges in Finland and Sweden, respectively.

Source	N tons/yr Finland	N tons/yr Sweden
Forest industry	5,500	1,700
Fertilizer industry	1,300	1,600
Other chemical industry	600	1,700
Mining, iron & steel industry	?	1,700
Textile and leather industry	500	?
Food processing industry	1,300	∿ 1,000
Total	∿ 9,200	> 7,700

It is obvious that both the Finnish and the Swedish figures contain great uncertainties, partly because important industrial branches has been omitted in each material and partly because the estimates of the contribution from the forest industry are very dissimilar.

Nitrogen discharges from forest industries

A somewhat closer look at the actual nitrogen discharges from the forest industry, therefore seems to be of great importance. The main interest regarding waste effluents from pulp and paper mills has since many years been devoted to their content of organic substances in solution or as suspended matter. Only recently, when important reductions of the discharges of oxygen-consuming, organic matter have been obtained, the occurrence of plant nutrients included in pulp and paper mill wastes have been focussed. Among the plant nutrients in these effluents phosphorus has been subject to some more comprehensive studies, reported in the literature. Therefore, at least some data on phosphorus releases from the forest industry are available (Bouveng and Hargbäck, 1971; Särkkä, 1974). As far as nitrogen is concerned, the estimates available in the literature are rather poor.

In many cases, the nitrogen in the effluents from pulp and paper mills occurs as organic nitrogen, i.e. in a form that is not directly available for the primary producers in the receiving body of water. Contrasting to this are of course those sulphite mills, which employ ammonia as base in the cooking liquor. From such mills considerable discharges of ammonium nitrogen may take place. In Sweden, only one mill is presently producing ammonia base pulp, but in e.g. the USA, about 20 % of the acid sulphite pulps manufactured (i.e. 700,000 tons/yr) are produced on ammonia base (Gehm, 1972).

The nitrogen discharges from ammonia base sulphite mills are in general in the order of 3-4 kg/ton of pulp. The only Swedish ammonia base mill recently reduced the discharges of nitrogen from about 350 tons/yr to about 175 tons/yr.

In order to obtain reliable estimates of the specific nitrogen discharges from the other branches of the pulp and paper industry, a series of analyses of the effluents from a total of 20 different pulp and paper mills have been collected. These analyses have been carried out as a part of the control programmes of the plants and are based on composed samples over a two-day period. Furthermore, the results are related to the actual production figures. The specific discharges are then expressed as g total nitrogen per ton 90 % dry product, see table 4.

TABLE 4

Specific Nitrogen Discharges in g/ton from Swedish Pulp and Paper Mills.

Production	Total nitrogen mean	range	N:o of mills surveyed
Unbleached sulphate	320	260-350	4
d:o + NSSC	110	50-170	2
Bleached sulphate	400	260-530	4
Unbleached sulphite	330	280-370	2
Bleached sulphite	620	-	1
Semi-chemical NSSC (NH_4)	1,700	-	1
Mechanical + sulphite & newsprint	140	80-220	5
Cardboard	150	140-160	2

Using the mean specific nitrogen discharges in table 4 in combination with the actual production figures for the different branches of the Swedish pulp and paper industry, a total nitrogen transport from this industry has been calculated. The figure obtained in this way amounts at 4,000 tons/yr. Although this probably is the hitherto best over-all estimate of the nitrogen discharge of a whole country, it must be stressed that it is based on rather crude mean values of the specific discharges. However, it might be assumed that the true figure is within ± 25 %.

In conclusion, Hansson's estimate of 1,700 tons/yr (see table 3), which he presented with the reserve that the real value could be about 3 times higher, apparently should be multiplied by a factor of 2.5. Of course, an even better estimate might be obtained if data from a number of additional mills are included in the calculation.

In most instances, the specific nitrogen discharges obtained in the survey and given in table 4 are lower than the estimates presented by Särkkä (1974), which were based on Finnish mills.

Fertilizer industry

The fertilizer industry is quite complex and a variety of types and grades of fertilizer materials are manufactured. The bulk of the aqueous waste load from the fertilizer industry, however, results from the preparation of a relatively few major products. Defining the volumes and compositions of the various waste streams is very difficult, because water recycle, minor process variations and operating philosophies can result in a wide range of waste stream compositions and volumes for a given product between different fertilizer plants. In addition, a great fraction of the total waste discharges is due to process spills, which are extremely irregular in frequency and size.

On the average, process water accounts for only 20-25 % of the water used by the fertilizer industry, but contains the bulk of the contaminants generated by the various processes. The waste streams can be divided into five general classes (EPA, 1971).

1. By-product streams
2. Scrubber solutions (from gas scrubbing equipment)
3. Process spills
4. Wash solutions (from equipment clean up)
5. Condenser water

An overview of the concentrations of the different nitrogen contaminants in the process waste streams from nitrogen fertilizer plants in the USA has been given in an EPA report (1971), see table 5. The very wide ranges are due to the sometimes used recycle of scrubber solutions, recovery of spills etc.

TABLE 5

Nitrogen Compounds in Process Waste Streams from Nitrogen Fertilizer Plants in the US.

Contaminant (mg/l)	NH_3 plant	NH_4NO_3 plant	$(NH_4)_2SO_4$ plant	Urea plant
NH_3	20-100	200-2,000	10-10,000	200-4,000
NO_3	-	50-1,000	-	-
Urea	-	-	-	50-1,000
Volume (l/ton prod.)	400-4,000	200-4,500	400-40,000	800-15,000

From a Swedish fertilizer factory, producing different types of nitrogen fertilizers and composed fertilizers (NP and NPK), the annual discharges of total nitrogen by the waste stream were, at the end of the sixties, 1,500 - 2,000 tons. In 1973, these losses were reduced to about 500 tons/yr (Landner, 1975). The reduction was primarily due to the construction of an ammonia recovery plant in the urea factory. Thereby it was possible to recover the ammonia formed by hydrolysis of the urea during the crystallization operation (Harstad, 1970).

From the two remaining fertilizer factories in the country, the total annual nitrogen discharges might not be above 300 tons. This would total the nitrogen transport from this industrial branch to approximately 800 tons/yr. It must be held in mind that the total quantity is in a very water soluble form and therefore easily available for the primary producers in the receiving bodies of water.

Iron and steel industry, metal finishing

The most important nitrogen discharges from these types of industries originate (1) from coke oven plants, sometimes linked with the iron and steel plants and (2) from pickling of stainless steel in nitric acid. The waste water from a coke oven plant might contain up to 15 g/l of ammonia. Such waters must be treated before recirculation or discharge, but the remaining amount of ammonia discharged with the effluents is in many cases considerable. In Sweden there is at the present time no such plant. The second great source of nitrogen pollution in the metal industry, production of stainless steel, is in return very important in Sweden. The annual production of stainless steel in this country is about 350,000 tons and this steel is pickled 2-4 times during the process. The pickling liquor generally consists of nitric acid and hydrofluoric acid. In 1971, the consumption of nitric acid for pickling purposes was about 8,900 tons. This corresponds to about 2,000 tons of nitrate nitrogen, most of which is lost to the sewer.

The so-called AX-process for recovery of metals and acids from a pickling bath has been introduced in at least one special steel plant in Sweden. This process would enable a recovery of > 95 % of the nitric acid from the spent liqour, and thereby almost eliminate discharges of inter alia nitrogen from the steel plant (Reinhardt, 1972).

In metal finishing a certain amount of ammonia and ammonium salts are used as well. The consumption of these nitrogen compounds might result in an annual nitrogen dicharge from the Swedish metal finishing industry of about 100 tons (SNV, 1972:4).

The total nitrogen discharge from the Swedish mine and metal industries, thus, would be in the order of 2,400 tons/yr.

Food processing industry

An estimate of the total contribution of the food processing industry to the nitrogen transport from industrial sources is very difficult to establish. This is due to the very great variations between different processing units, and also to the fact that many minor installations are connected with the municipal sewer system. Therefore, a certain part of the discharges from the food processing industry is already included in the figure for municipal discharges. The types of food processing industries, the effluents of which may contain particularly high concentrations of nitrogen compounds are slaughter houses, dairies, fermentation industries, beet processing industries etc. The removal of nitrogen from these waste waters could in principle be carried out according to similar methods as those used for municipal sewage. Some alternative methods for nitrogen removal from waste water are presented in table 6, according to Eliassen and Tchobanoglous (1968).

TABLE 6

Waste Water Treatment Processes Used for Nitrogen Removal.

Process	Classification	Removal efficiency %
Biological treatment	B	30-50
Anaerobic denitrification	B	60-95
Algae harvesting	B	50-90
Ammonia stripping	C	80-98
Ion exchange	C	80-92
Electrochemical treatment	C	80-85
Electrodialysis	C	30-50
Reverse osmosis	P	65-95
Distillation	P	90-98
Land application	P	-

B = biological; C = chemical; P = physical.

The cost spectrum of these methods is extremely wide.

Due to the difficulties discussed above, it has not been possible to arrive at any good estimate of the nitrogen contribution from the food processing industry in Sweden. A rough guess would give us a figure in the order of 500-1,000 tons/yr.

Summing up

A summary of the actual industrial nitrogen discharges in Sweden, using the best estimates available to the author, should lead us to a slight revision of the last column of table 3. The result is shown in table 7.

TABLE 7

Revised Estimates of Annual Industrial Nitrogen Discharges in Sweden

Source	N tons/yr	%	Reference
1. Forest industry	4,000	39	Present work
2. Fertilizer industry	800	8	" "
3. Other chemical industry	1,700	16	Hansson (1975)
4. Mining, iron & steel industry	2,400	23	Present work
5. Textile and leather industry	500	5	Särkkä (1974)
6. Food processing industry	1,000	9	Hansson (1975)
Total	10,400	100	

Further studies, in order to increase the quality of the estimates for lines 3, 5 and 6 are obviously needed. As far as food processing and textile industries are concerned, those installations, which are connected with municipal sewage treatment plants should be accounted for separately.

If the industrial contribution of the nitrogen transport to Swedish surface waters is set to 10,000 tons/yr and the municipal contribution to 17,000 tons/yr (Thorell and Carlsson, 1975), the relative importance of the various sources will be as shown in table 8. The remaining figures are taken from Ahl and Odén (1974), whose table 7 is partly revised.

TABLE 8

Sources of Nitrogen Transport to Surface Waters in Sweden

Source	N tons/yr	N %
Background	58,000	44
Forest drainage	2,000	1
Agricultural drainage	45,000	34
Municipal wastes	17,000	13
Industrial wastes	10,000	8
Total	132,000	100
Human sources	74,000	56

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