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MERCURY LOSSES FROM CHLOR ALKALI PLANTS

THE CANADIAN EXPERIENCE

Transmitted by the Government of Canada

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Background

In 1968 an investigation conducted in the Canadian Prairies showed that wildlife, in regions where the growing of grain from mercury treated seed was common, contained elevated levels of mercury.

Major attention on the emerging mercury problem was focused when, in November 1969, fish taken from the South Saskatchewan River Drainage Area were found to contain up to 10 ppm mercury. During the following months several other areas were found to be contaminated and large amounts of commercially caught fish were impounded and destroyed. Sixteen water bodies were closed either totally or partially to commercial fishing and a national inspection programme was instituted to ensure that fishing products reaching the market were safe.

Appended to this paper is a map of Canada showing the locations of the mercury cells chlor-alkali plants in operation in early 1970, and the fishing areas which were either totally or partially closed.

Table I below summarizes, by industrial sectors, the use of mercury in Canada during the year 1969.

It should be noted that, except for the paints, the figures shown represent mercury used and released in one way or another to the environment. In the case of paint figures represent the total mercury used in the manufacturing of paints for both Canada and export.

Chlor-alkali plants accounted for more than 47% of the total mercury used and, being point discharges, were by far the most important sources of mercury to water environment.

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Table I

Mercury Consumption in Canada
(in metric tons)

	1969
chlor-alkali	130*
paints	18
electrical apparatus	15
control instruments	14
dental applications	12
agriculture	12
general laboratory use	9
pharmaceuticals	1
pulp and paper	1
other	62
TOTAL	274

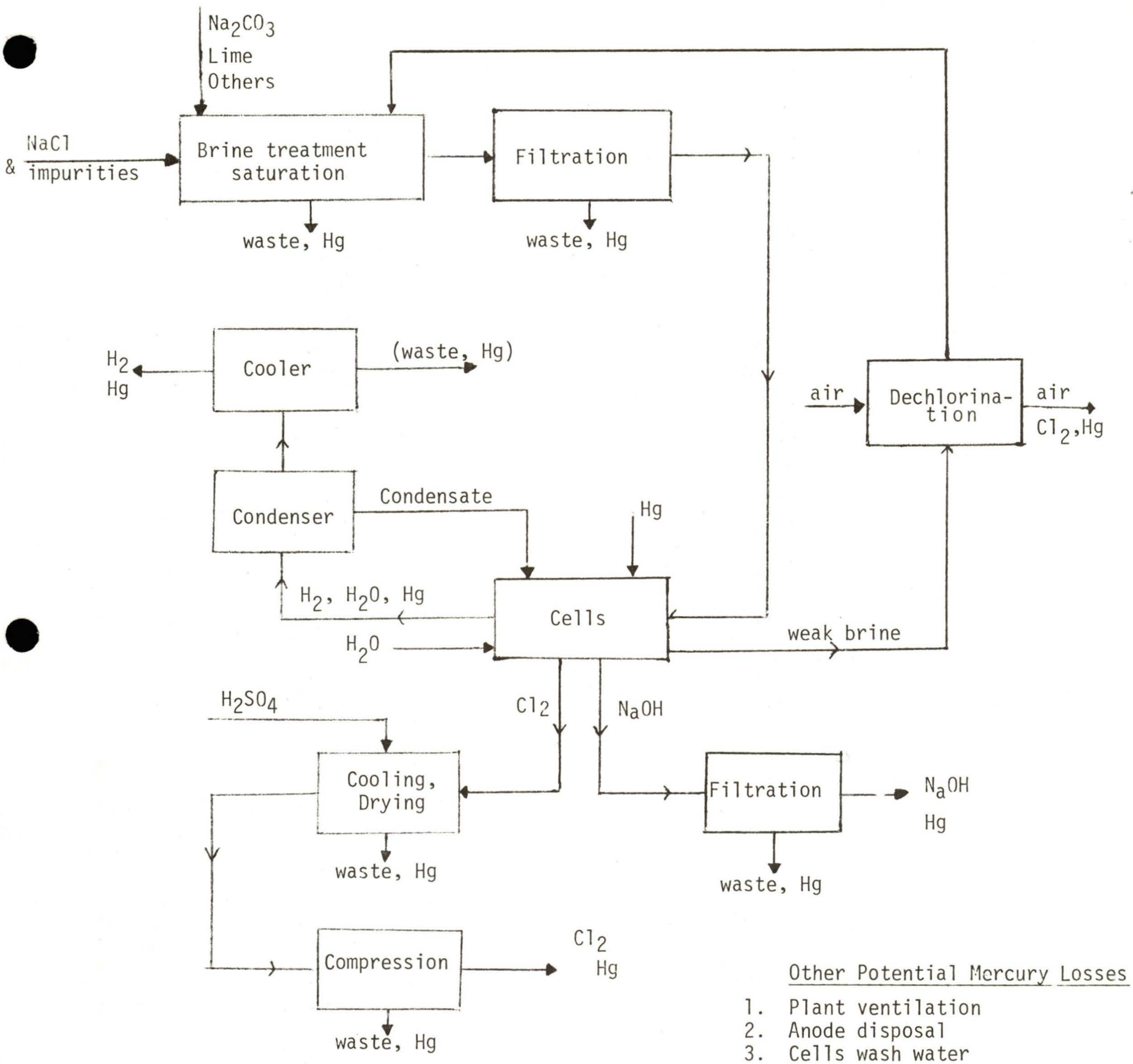
*Consumption and new equipment

Table II

General Information and Mercury Losses from Canadian Mercury Cells Plants Prior to Control Measures

	1969	1970
Number of plants	14	15
Chlorine production	480,000 ST	485,000 ST
Capacity range	40-250 STPD	

	Losses in lb/day/100 $STCl_2$
- with products	
NaOH	0.2-14
Cl	0.01
- with sludges	
brine regeneration & purification	0.2-20
- with waste waters	
floor wash and other	3-30
hydrogen coolers	0-20
- with atmospheric emissions	
hydrogen	2-40
cell room ventilation	0.2-9
end boxes ventilation	0.2-2
- Other	9



Other Potential Mercury Losses

1. Plant ventilation
2. Anode disposal
3. Cells wash water
4. Floor sweeping
5. Waste waters

Figure I. MERCURY CELL FLOW DIAGRAM AND POTENTIAL SOURCES OF MERCURY LOSSES

Figure I shows schematically the main potential sources of mercury losses from a typical mercury cells plant producing chlorine and sodium hydroxide. For simplicity, only the main equipment or group of equipment are indicated. Mercury losses occur:

- with waste waters - from spills, plant cleansing procedures, hydrogen cooling etc.;
- with sludges - from brine regeneration and filtration and in the eventual purification of caustic soda;
- with process products - caustic soda, chlorine, hydrogen
- with atmospheric emissions - from cells room ventilation, hydrogen venting, end boxes venting etc.

In 1969, prior to control measures, we had fourteen plants producing chlorine with mercury cells; their average daily capacity was approximately 1,500 short tons of chlorine and their capacity range was 40 to 250 tons. Chlorine production in 1969 was 480,000 short tons and the mercury consumption in the order of 239,000 pounds. Additional 47,000 pounds were used in stocking new cells. Table II shows some general information on Canadian plants prior to control measures. Mercury losses are referred to a production of 100 short tons of chlorine per day; mercury was lost with products, sludges, waste waters, atmospheric emissions and other; the wide ranges shown indicate the variation in plants type, age, supervision and other factors affecting mercury consumptions. On the average during 1969, for every 100 short tons of chlorine produced 0.498 pounds of mercury were consumed.

Approximately 62% of the mercury lost ended directly into water streams amd the remaining 38% was assumed lost to atmosphere, products and soil.

The table represents a good estimate of losses which, not monitored at the time they took place, were arrived at from measurements taken in early 1970 and from knowledge of the total mercury consumed.

Control Measures and Results

In December 1970 the Federal Minister of the Environment asked the chlor-alkali industry to voluntarily control mercury losses while appropiate legislation was being prepared. While industry started to work immediately regulations for the discharge of mercury from chlor-alkali plants were promulgated in early 1972.

Since 1972 each chlor-alkali plant using mercury cells is required:

- to limit discharges to water to 0.005 pounds per short ton on chlorine produced
- to monitor and sample (proportionally to flow) its water effluents
- to maintain records of
  a) mercury purchased for any purpose
  b) mercury used, disposed of or stored
  c) mercury present in each liquid effluent leaving the plant
  d) quantity of each effluent discharged
- to submit such records to the Federal Authorities

The chlor-alkali mercury regulations were promulgated under the Fisheries Act, an Act which provides that no substance or water shall be deposited in waters frequented by fish if such substance or water is harmful to fish or to the use by man of fish.

Measures taken to control mercury losses ranged between two extremes; from the disposal of contaminated waters and sludges into deep wells, to the phasing out of the mercury cells plants themselves in favour of the diaphragm cells. Some plants made a real effort not only to comply with the law but also to minimize all mercury emissions to water, atmosphere and soil.

In general, every chlor-alkali plant segregated and stored mercury contaminated sludges and solids and took steps to minimize water uses in order to reduce the waste waters volume. Contaminated process waters and uncontaminated cooling waters were segregated and sent to separate drains.

Other common control measures taken were:

- removal of mercury from waste waters by precipitation with sodium bisulphide, flocculation and filtration. In this way the mercury concentration in the final effluent could be reduced to less than 0.1 ppm.
- indirect cooling of the hydrogen stream to or below 60^{0} F and separation of entrained mercury droplets
- dewatering and disposal of brine sludges (some containing up to 2,000 ppm of Hg)
- filtration of caustic soda
- prevention of air leaks from equipment

In one instance, at the FMC plant at Squamish, British Columbia, the company took the following steps:

- combination of water recycle, sulphiding and mercury recycle from both liquid and solid wastes;
- minimization of atmospheric emissions, scrubbing of end-box vents and cooling of hydrogen to 60°F;
- careful housekeeping;
- neutralization of final effluent and destruction of residual chlorine.

Table III shows a typical effluent from the FMC plant.

Table III

Total Flow	5-6	$x10^6$G/D
Suspended Solids	5	ppm
pH	6.7 - 7.5	ppm
Chlorine	0.08	ppm
Hg	0.003	ppm
Temperature	50-80	°F

The total mercury purchased by FMC for addition to the cells, that is the total mercury consumed, is in the order of 0.03 pounds for short ton of chlorine produced. This figure has been confirmed by two years of data.

Bioassay tests conducted at the plant showed 100% fish survival in 96 hours exposure to 100% effluent.

The total cost of the control measures was, in 1971 dollars, approximately $700,000 and operating costs were approximately $90,000 per year.

The FMC's plant at Squamish is an example of what we consider best practicable technology in treatment of effluents from a mercury cells plant.

Except for conversions to diaphragm plants, the cost of control measures taken by Canadian plants ranged between $40,000 and $1,000,000 depending upon the size of the plant, its location and its particular problems.

In a period of twelve months ending July-August 1973, there were thirteen mercury cells plants operating in Canada, two others were shut down in favour of a new diaphragm cell plant. In this period 104,000 pounds of mercury were added to the cells to produce 425,000 short tons of chlorine. The hystogram on Figure 2 shows the rate of mercury consumption by the thirteen plants. On the average 0.244 pounds of mercury were consumed for each short ton of chlorine produced, this figure compares with 0.498 pounds prior to control measures. It should be noted that one fourth of the total production was obtained by consuming only 0.033 pounds per ton.

Figure 3 compares mercury losses prior and after control measures.

By July-August 1973 losses to water were reduced, for a twelve months period to 2,080 pounds, to be compared with 148,000 pounds prior to controls. Since early 1973 such losses were further reduced and for the twelve months period ending December 1973 they should be in the order of 850 pounds or less than 0.6% of the total consumption during 1973.

Our estimates are based on the records received during 1973.

Losses to atmosphere represent the measurements and estimates submitted by each plant. They include losses due to cell room ventilation, end boxes vents and hydrogen vents. Work is presently underway to measure or improve the estimate of atmospheric losses and to develop regulations limiting emissions to the atmosphere.

One other interesting point is the amount of mercury which was not accounted for by the companies but was still consumed in the process. It gives an indication of the difficulties of attempting a mass balance in a chlor-alkali plant. Four of our plants have accounted figures in the range of 16% to 26%, which indicates that mass balances from the remaining plants could be further improved.

Conclusions and Future Action

One effect of the control measures taken has been a reduction of the mercury used per unit of production from 0.498 to 0.244 pounds per short ton of chlorine; this amounts to a reduction close to 48%.

A mass balance of the mercury used in the chlor-alkali process presents several difficulties. Approximately 75 to 80% of the total mercury consumed could be accounted for and additional work should be done to identify how the remaining 20 to 25% is consumed.

An appreciable amount of mercury is still consumed by Canadian plants in the manufacturing of chlorine. A further reduction in mercury consumption could be possible with some recovery of the mercury now present in sludges and solids waste.

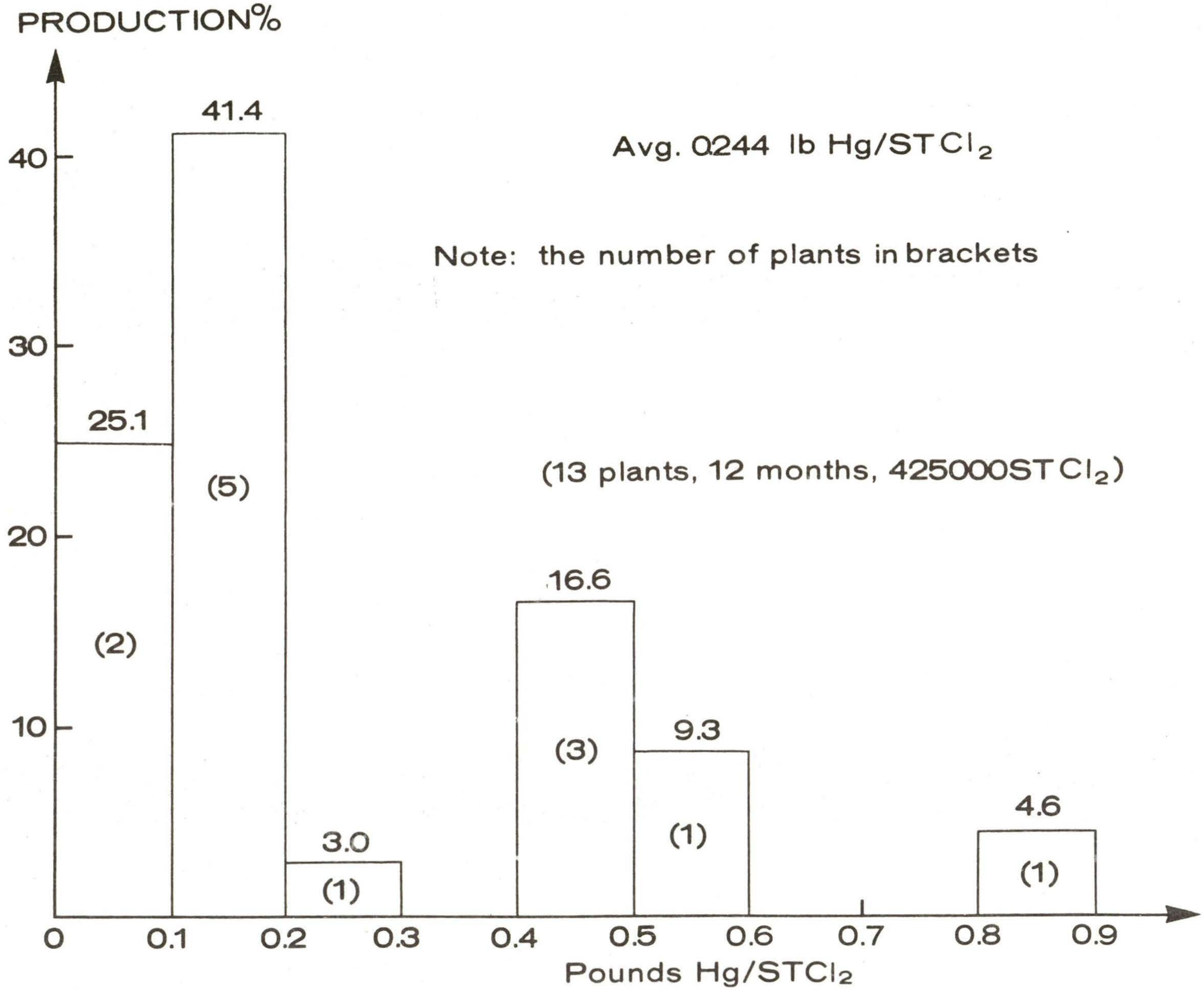
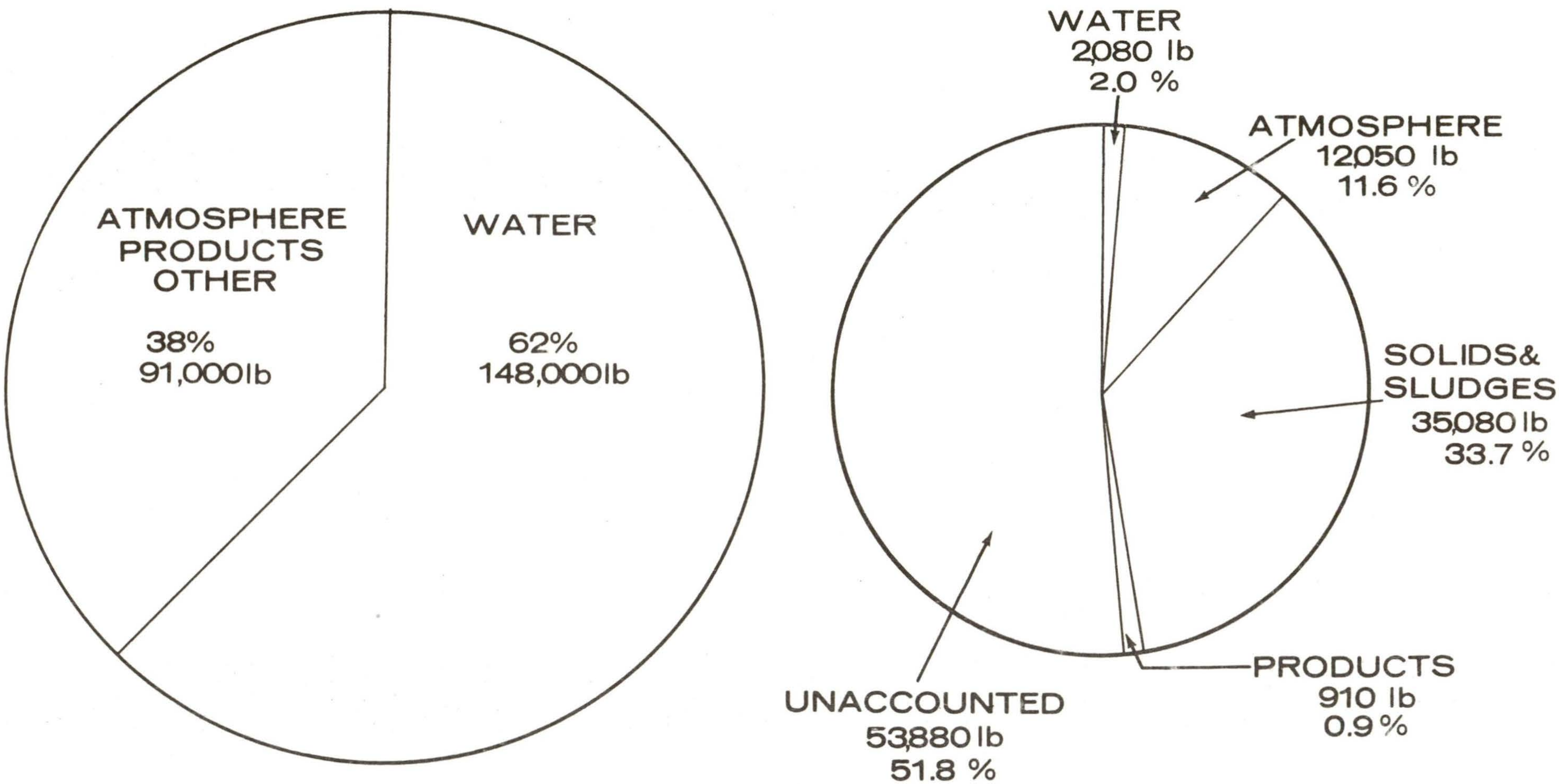


Figure 2 Mercury Consumption after control measures

Prior to control measures
(12 months)

After control measures
(12 months ending July-August 1973)



Total Hg consumed 239,000 lb
Chlorine produced 480,000 tons

Total Hg consumed 104000 lb
Chlorine produced 425000 tons

Figure 3 Break down of mercury losses prior and after control measures.

Considering all sources of mercury pollution in Canada, losses to water streams by Canadian chlor-alkali plants have been reduced to a minor amount; they will be further reduced through the continuous improvement of the equipment used and its supervision.

Mercury in solids and sludges is presently contained in ponds or buried. Measures are taken to avoid its escape which could create new water or soil pollution.

Work is underway to measure or improve the estimate of losses to atmosphere and to develop regulations limiting emissions to the atmosphere.

Next year, after analyzing the residual losses to water, atmosphere, soil and products we will make a good forecast of the mercury losses from our chlor-alkali plants in the future years. If, in relation to all Canadian sources of mercury pollution we identify the need for further control measures, such measures will be taken.

References

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  The Experience of Japan, Sweden, Canada and USA. (1973)
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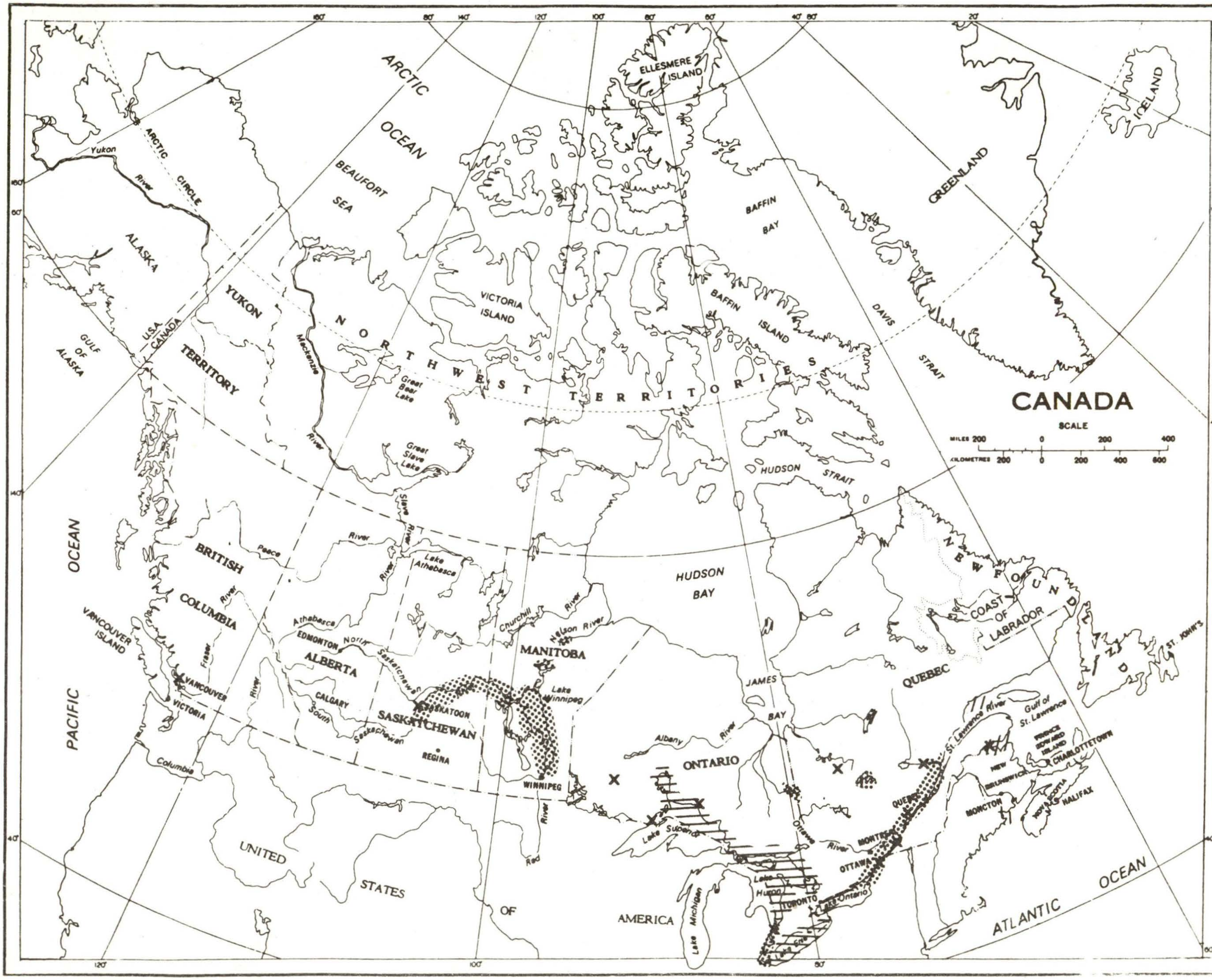
Location of Canadian Chlor-Alkali Plants and Commercial Fisheries Affected by Mercury Pollution



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