

APPENDIX F-1

**Comments regarding the Northern Pulp, Nova Scotia
Environmental Assessment Registration Document.
Replacement Effluent Treatment Facility**

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The following are comments with regard to the Environmental Assessment (EA) Registration documents submitted in support of the Northern Pulp effluent treatment proposal.

By way of introduction, please find my curriculum vitae attached to this report. I am trained in chemical engineering, applied chemistry and biochemical engineering (doctoral level). I have subsequent experience examining toxicants in environmental and human health, and regulatory issues; clinical epidemiology / medical research; research specifically into arsenic, cadmium, lead and mercury; and have published in the peer-reviewed literature on biosorption of toxic metals, as well as health effects of toxicants and medical approaches to environmentally-linked disease in clinical practice. I have examined environmental toxicants and human health in a number of situations and locations, ranging from chemicals used at CFB Galetown, to air quality in the Peace River district of Alberta. I have also worked in modelling enhanced oil recovery, which is similar to but more complex than hydrology, and is relevant in consideration of groundwater flows.

My comments regarding the current Northern Pulp EA are limited due to the short timeframe within the selected Nova Scotia process. I would have provided a more fulsome review of a more comprehensive selection of topics, if more time had been available. I am focusing on what I consider to be some important gaps and shortcomings in the information provided, and the issues considered. In the present case, omission by NPNS and its consultants of topics for consideration, and presentation of incomplete or unreliable information can lead to under-estimation and lack of consideration of potential harms. Decision-making on this EA, in the absence of a more complete submission from NPNS, could result in missed opportunities to make wiser choices and to avoid future harms and liabilities, and could result in further (potentially preventable) future harms.

In response to the EA Registration documents, I herein:

1. comment briefly on section 9, pertaining to scoping of a potential future human health review;

2. address implications and reports of specific toxicants (mercury, cadmium, reduced sulphur compounds [RSCs] and polycyclic aromatic hydrocarbon [PAH] chemicals, including chlorinated dioxins and furans); and in this context
3. broaden consideration to include sensitive and directly applicable human and environmental health indicators and effects.

In summary, the current Environmental Assessment lacks:

- Data and analysis regarding some unmentioned and unaddressed hazards, particularly mercury, associated with the Canso Chemicals Ltd. legacy landfill as well as mercury spilled into bedrock beyond the landfills. This includes an underground mercury plume, and related risks to drinking water and the surrounding environment, biota and all who may consume affected foods. Precise locations are unclear and the Canso legacy is not mentioned in EA Registration documentation, but the landfill abuts or overlaps the proposed effluent treatment facility;
- Sufficient information to establish baseline environmental conditions in terms of mill operations and emissions (in part because the oxygen delignification equipment, a key component promised to the public, and important for pollution reduction, is not yet in place), as well as contamination of the environment, ecosystems and foods;
- Sufficient information to establish baseline health and contamination of the surrounding lands, water, biota and populations.

In the absence of necessary data and analyses, the current EA is incomplete. In the absence of information, the Minister cannot make a decision with confidence that the proposed Effluent Treatment Plan will not result in serious harms to the environment, or to people living and working in the area. The Minister cannot ensure that necessary baseline data and surveillance are in place for early alerts to increasing toxicants or ecological changes. Any approvals would appear to be ill-informed and premature at best.

Section 1. Comments on EA registration document section 9, regarding scoping of a potential human health risk assessment (HHRA), or a human health evaluation (HRA)

Section 9 of the EA registration document, “Human Health Evaluation” is 31 pages long, describing what a human health risk assessment (HHRA) might consider, and arguing for exclusion of considerations on the basis of supposed irrelevance. Should a HHRA be required in the future, this section argues for a narrow scope in terms of:

- chemicals of potential concern;
- populations;
- potential effects related to the proposed waste water treatment project; and
- issues that arose historically.

NPNS is seeking an overly narrow scope for the assessment. This approach is not acceptable, as it would fail to address significant issues, including but not limited to:

- scoping is argued in the context of a proposed mill (Toxikos, 2006), that did not have the history of and location on a site with pre-existing toxic chemicals (this mill was never built);
- the fact that air emissions and effluent composition will not be known with certainty until after the NPNS mill equipment is updated, new equipment is installed, and burning of sludge is implemented;
- lack of analyses of anticipated sludge composition, and effects on air emissions of toxic metals and polyaromatic hydrocarbons (PAHs);
- omission of the foetus and pregnant mother as a population of concern;
- the fact that historical issues such as mercury, and PAH (including dioxin and furan) contamination will continue for extended periods of time; and
- contaminant analyses of foods available on the land and in the waterways and ocean.

Section 2. Comments on EA registration document sections reporting environmental contaminants mercury, cadmium, reduced sulphur compounds and polyaromatic hydrocarbons (including dioxins/furans)

Mercury

Mercury, including methylmercury, is an established developmental and neurological toxicant, and is recognized as a global pollutant for action under the Minimata Convention. Canada has ratified the Minimata Convention. Methylmercury, the common form of organic mercury, is formed via microbial action, under oxygen-poor or anaerobic conditions such as in wetlands and sediments. Methylmercury is lipophilic (“fat loving”), so it accumulates in fatty tissues. Methylmercury in fish and other aquatic organisms poses risks to fishers, and individuals and communities relying upon these foods. Other forms of mercury (vapour and salts) are also highly toxic.

Mercury was historically essential to the process to generate the chlorine and sodium hydroxide that were used to bleach pulp, in “chlor-alkali” plants. Mercury pollution is well known for being associated with chlor-alkali plants at Canadian pulp mills. Mercury in waterways such as the English-Wabigoon river system in Ontario has debilitated generations of Aboriginal peoples.¹ Most chlor-alkali plants were closed during the 1970s,² but Canso Chemical Ltd. operated through the 1980s.³ Appendix I1-B in the EA Registration package indicates that with the closure of Canso in 1992, “Generation of mercury and dioxins & furans from chlor-alkali process ceases.” Unfortunately, concerns regarding these persistent toxicants linger to this day.

Mercury contamination exists at the Northern Pulp Site

A Statutory Declaration by John Daniel Currie, dated July 8th, 1997, reveals that Canso Chemicals Ltd. operated a chlor-alkali plant and associated landfills at Abercrombie Point, on a property approximately 23.29 acres in size, abutting the Northern Pulp Mill site and immediately adjacent to the site of the proposed Effluent Treatment Facility. The Canso Chemicals Ltd. Decommissioning Final Report (Attention Mr. Dan Currie, January 26, 2000) indicates that mercury infiltrated the bedrock more than eight metres below the room where the mercury cells produced chlorine gas and alkaline water. Thus, substantial quantities of mercury apparently remain on the site, in landfills created to hold wastes during operation and subsequent demolition, on the site of the demolished Canso buildings, and in the bedrock.

The location, condition and contents of the mercury-containing Canso site would have to be confirmed, to avoid further releasing mercury into the local environment during construction of the new effluent treatment facility, via disturbance of landfills, or as a result of alteration of groundwater flow and drainage. Groundwater in the area should be monitored, with a view to intercepting mercury contamination as it spreads.

The Decommissioning Report speculated (perhaps optimistically) that the mercury plume would eventually (in perhaps, approximately 200 years) emerge underwater in Pictou Harbour. That said, it is acknowledged that the mercury might surface sooner, closer to its source, potentially affecting the shoreline and wetlands, and presumably groundwater quality en route. **Vagaries of fractured bedrock make it virtually impossible to predict mercury migration, so to protect neighbours' drinking water and to anticipate impacts on the environment and marine food sources, it is important to investigate migration of the mercury plume, and biological receptors within the landscape that may accumulate mercury (e.g., wetlands species and shellfish).** This should be an essential component of any EA process.

Importantly, albeit without having examined existing detailed geological investigations should they exist, I wish to flag the possibility that the mercury plume may intercept wells in the neighbourhood. If the plume intercepts one well, there is potential for contamination of several wells, via contamination of any aquifer that is common among wells. With fractured bedrock, it is not necessarily the case that the closest wells would be affected first. Hydrogeological testing and well water testing would have to be carried out.

Wherever the mercury plume encounters pulp mill effluents or organic materials, methylmercury might be formed.

Among dozens of metals and other chemicals, mercury and methylmercury were *not* measured in the assessment (Appendix M4 – Surface Water Data, Dillon). It is surprising that mercury was omitted from the report, as mercury (and

methylmercury) would typically be a standard element in a large panel of environmental analyses such as is reported in Appendix M4.

Lack of analyses of mercury species is a serious omission, given that:

- **mercury is an important toxicant in any environmental assessment of an old pulp mill that previously hosted a chlor-alkali plant on site. Contamination may spread into ground- and surface water, and may enter effluent during treatment;**
- **methylmercury is a well known contaminant of aquatic species, posing risks throughout the food chain. Populations along the coast may be high consumers of these foods, posing risks to all ages and particularly to unborn children;**
- **there is a history on this site of mercury contamination remaining in landfills and the bedrock, from Canso Chemicals Ltd. Mercury contamination is documented in the immediate area of the proposed effluent treatment facility. The current status of this mercury plume is undisclosed. Disturbance of mercury containing landfill, soils and rock during construction and operation may accelerate toxicant mobilization and amplify harms to environmental and human health;**
- **there was a well publicized, third party report of mercury in the immediate area (e.g., <https://www.capebretonpost.com/news/local/report-shows-heavy-metals-in-pulp-mill-effluent-7486/>);**
- **as the regulator, and recipient and custodian of all documentation, Nova Scotia Environment should be well aware of this history; and**
- **Dillon Consulting prepared both the final decommissioning report for Canso Chemicals Ltd., as well as the EA documents for Northern Pulp, so clearly should have been aware of the issue.**

Cadmium

Cadmium is a highly toxic heavy metal that occurs naturally, and can be accumulated from the soil by plants. Cadmium is at elevated concentrations in pulp mill effluent, because the naturally occurring element is concentrated from high volumes of biomass. Cadmium also bioaccumulates in liver, kidney and bone, building up with age. Toxicologically, cadmium is somewhat similar to, but much more potent than lead (environmental quality standards for water and air are typically 10 to 100 fold lower for cadmium than for lead). According to the International Agency for Research on Cancer (IARC) cadmium is a probable human carcinogen.⁴ Among numerous other health effects, cadmium is toxic to the developing child, affects multiple organ systems including the kidneys, liver, and cardiovascular system, disrupts the endocrine (hormone) system, and weakens bones.^{5,6,7,8}

Cadmium may accumulate in wildlife, including fish and crustaceans, and is the reason for consumption restrictions for wild foods such as shellfish, and organ meats. ^{9,10}

It is claimed in section 9 that cadmium has not been detected in NPNS emissions. The spreadsheet of 2017 analyses of water from the Boat Harbour Raw Effluent Ditch, (author Wayne Williams), indicates that the detection limit for cadmium was 0.01 µg/L, which is identical to the provincial ecological criterion for surface water. Thus, the cadmium analyses would not detect levels below the ecological criterion. In fact, cadmium may be of limited solubility in these waters, and should be monitored in particulates and sediments. Of note, this is consistent with shellfish being particularly susceptible to contamination.

Table 1 summarises cadmium levels in “watercourse” samples, as reported in Appendix M. Cadmium at WC05 was at levels almost an order of magnitude higher than elsewhere (cadmium was also elevated at WC03). Levels at WC03 and WC05 exceeded Canadian Water Quality Guidelines (Table 2) for the protection of aquatic life, both for fresh and marine waters. I did not identify a map of these locations, but apparently these lowest numbered samples are closer to and may be more likely to be impacted by NPNS.

I bring up the topic of cadmium in the absence of definitive evidence in the data presented that it is of high impact in this particular instance. Rather, cadmium is a highly toxic element, is expected to be a significant issue in this instance, has not been sufficiently investigated with regard to NPNS, and bears investigation as part of any EA.

Table 1. Cadmium levels (µg/L) in watercourse samples, December 3, 2018. (ref. Appendix M4)

Location	Cadmium concentration (µg/L)
WC16	0.037
WC15	0.056
WC14	0.024
WC13A	0.018
WC13B	0.017
WC12	<0.01
WC11	0.033
WC10	0.019
WC09	0.05
WC08	0.032
WC06	0.041
WC05	0.43
WC03	0.23

Table 2. The Canadian Water Quality Guidelines (CWQG) for the protection of aquatic life for cadmium

	Long-term Exposure (µg/L)	Short-term Exposure (µg/L)
Freshwater	0.09 ^a	1.0 ^b
Marine	0.12	NRG

NRG = no recommended guideline

a The long-term CWQG of 0.09 µg·L⁻¹ is for waters of 50 mg CaCO₃/L hardness. At other hardness values, the CWQG can be calculated with the equation $CWQG = 10_{\{0.83(\log[\text{hardness}]) - 2.46\}}$, valid for hardness between 17 and 280 mg CaCO₃/L

b The short-term benchmark concentration of 1.0 µg·L⁻¹ is for waters of 50 mg CaCO₃·L⁻¹ hardness. At other hardness values, the benchmark can be calculated with the equation $Benchmark = 10_{\{1.016(\log[\text{hardness}]) - 1.71\}}$, valid for hardness between 5.3 and 360 mg CaCO₃/L

Hydrogen Sulphide

Hydrogen sulphide, with its characteristic “rotten eggs” smell, is the simplest of a group of chemicals called “reduced sulphur compounds” (RSCs), also reported as “total reduced sulphur” (TRS). Other RSCs include carbonyl sulphide and carbon disulphide that do not have strong smells, as well as mercaptans and others that do have strong odours (a trace quantity is used as an alert chemical in natural gas). RSCs are the compounds largely responsible for the odour of pulp mills.

RSCs are sometimes characterized inaccurately as mere nuisance odours, but they are in fact toxic to the nervous system and to multiple organs.¹¹ Acute, episodic exposure to malodorous sulphur air pollutants released by a pulp mill causes breathing difficulties, and other respiratory, ocular (eye) and neuropsychological symptoms.¹²

Larger RSC molecules may be longer acting than simple hydrogen sulphide. Numerous reduced sulphur compounds exert substance-specific toxicities, but then are ultimately metabolized to create hydrogen sulphide, so they can all also have similarly toxic effects in the body. These include multi-system adverse effects, with life-long implications for the foetus and developing child (e.g., irritation of eyes, nose and throat, cough, headache, fatigue and malaise, nausea and vomiting, and headache, confusion and depression, and effects on the central and peripheral nervous system with chronic exposure).^{11,13}

Pulp mill emissions of RSCs contain many more chemicals, and greater quantities of reduced sulphur, than may be measured or estimated as hydrogen sulphide *per se*. If this is true in the present case, the analyses reported in the EA Registration package (reproduced below) may under-estimate the load of reduced sulphur, and thereby its biological effects.

A 2017 study by Hoffman et al.^{14, 1} was extensively discussed in the Environmental Assessment document (section 8.1.2.2). The Hoffman report clearly indicates, using straightforward treatment of routinely gathered data, that some toxic volatile chemicals measured in Pictou probably originate at the Northern Pulp facility. The data is from routine Canadian pollutant monitoring as well as weather data.

Northern Pulp monitoring reports posted on the Nova Scotia website, and modelling in the EA Registration package, all indicate exceedances of hydrogen sulphide or RSCs. These exceedances are predicted to continue with the new effluent treatment facility. The following tables, reproduced from the EA Registration package, indicate that hydrogen sulphide has been and is expected to continue to exceed permissible concentrations.

AIR DISPERSION MODELLING STUDY – REPLACEMENT EFFLUENT TREATMENT FACILITY

January 21, 2019

Hydrogen Sulphide

The maximum predicted ground level concentrations for hydrogen sulphide (H₂S) at each discrete receptor are presented in Table 6.5.

Table 6.5 Maximum Predicted Ground Level Concentrations (GLC) for H₂S – Existing

Receptor ID/Regulatory Limit	UTM Coordinates		1-hour (µg/m ³)	24-hour (µg/m ³)
	Easting (m)	Northing (m)		
Regulatory Limit	-	-	42	8
1	519768	5055219	20.4	0.86
2	520907	5053346	18.1	1.16
3	522480	5053951	7.69	0.77
4	522963	5054415	40.5	2.69
5	522899	5054854	37.0	2.55
6	524552	5055699	96.6	4.90
7	524337	5056312	34.8	2.21
8	526942	5057565	15.4	1.46
9	528826	5055486	2.52	0.24
10	522169	5058110	2.21	0.58

Bold – indicates an exceedance

Exceedances of the Nova Scotia maximum permissible ground level concentration limit for H₂S for the 1-hour averaging period were predicted at discrete receptor 6. The source contributing to the exceedance at discrete receptor 6 is the existing ETF. There were no exceedances of the 24-hour maximum permissible ground level concentration limit.

Further analysis of the above modelling results, including a exceedance frequency analysis at receptor 6, are discussed in Section 7 below.

¹ This study is found at Appendix E-2 of the Friends of the Northumberland Strait/Ecojustice submission, along with a response at Appendix E-1, from Ms. Hoffman to Stantec’s critique in the NPNS EA submission.

Hydrogen Sulphide

The maximum predicted ground level concentrations for hydrogen sulphide (H₂S) at each discrete receptor are presented in Table 6.11. No exceedances of the Nova Scotia maximum 1-hour permissible ground level concentration limits were predicted for H₂S. For the 24-hour time averaging period, the maximum predicted concentration of H₂S at Receptor 5 was slightly above the maximum permissible ground level concentration limit.

Table 6.11 Maximum Predicted Ground Level Concentrations (GLC) for H₂S - Future

Receptor ID/Regulatory Limit	UTM Coordinates		1-hour (µg/m ³)	24-hour (µg/m ³)
	Easting (m)	Northing (m)		
Regulatory Limit	-	-	42	8
1	519768	5055219	9.46	1.89
2	520907	5053346	10.4	2.01
3	522480	5053951	12.2	2.66
4	522963	5054415	18.0	4.40
5	522899	5054854	21.3	8.52
6	524552	5055699	2.15	0.75
7	524337	5056312	10.6	2.50
8	526942	5057565	7.21	1.14
9	528826	5055486	1.08	0.23
10	522169	5058110	1.59	0.61

Bold – indicates an exceedance

Further analysis of the above modelling results is presented in Section 7 below.

Table 7.1 Emission Impact Summary Table - Existing Operation

Contaminant	Maximum Predicted Concentration at Nearby Specific Receptors (µg/m ³)	Averaging Period	Reference Criteria* (µg/m ³)	Percentage of Criteria (%)
Carbon monoxide (CO)	340	1-hour	34,600	1%
	200	8-hour	12,700	2%
Hydrogen sulphide (H ₂ S)	96.6	1-hour	42	230%
	4.9	24-hour	8	61%
Nitrogen dioxide (NO ₂)	29	1 hour	400	7%
	0.78	Annual	100	1%
Sulphur dioxide (SO ₂)	57.3	1 hour	900	6%
	11.1	24 hour	300	4%
	0.68	Annual	60	1%
Total suspended particulate (TSP)	51.1	24-hour	120	43%
	3.35	Annual	70	5%
PM _{2.5}	7.92	24-hour	28	28%
	0.68	Annual	10	7%

*The criteria for the listed contaminants are Maximum Permissible Ground Level Concentration Limits specified in the Nova Scotia *Air Quality Regulations* except for PM_{2.5}, which criteria are Canadian Ambient Air Quality Standards.

These results, copied from the EA Registration package, indicate both past and projected exceedances of hydrogen sulphide exposures. One might think that prediction of reaching a high proportion, let alone exceedances of air pollution guidelines, would send proponents back to the drawing board. This was not the case. Following these reports and predictions of excessive levels of RSCs, it is explained not that these are the result of the pulp mill, but that these are the result of abnormal weather conditions or “meteorological anomalies.” It is then recommended that these may be ignored. The nature of anomalies is not detailed, but could include situations such as temperature inversions that impede atmospheric mixing. The consultants then explain that by using the 9th highest hourly concentration rather than the highest concentration in modelled years (i.e., previously observed “extremes” are removed), the hydrogen sulphide levels are predicted to be within compliance at a residential area close to the existing effluent treatment facility. The report concludes that although hydrogen sulphide exceedances are modelled, that with elimination of meteorological anomalies it is anticipated that exceedances will not be experienced.

It is unreasonable and certainly not precautionary, particularly in this era of climate change, to base environmental assessments on assumptions that “meteorological anomalies” will not repeat. Indeed, with weather anomalies of all kinds becoming more frequent and extreme, the opposite is expected, and should be assumed and factored into assessments.

Furthermore, approving and thereby facilitating periodic exceedances of health-based exposure criteria, for communities that include the most vulnerable of individuals and who are more susceptible to adverse effects, is contrary to the purpose of limits, and the mandate to protect public health. Process changes for pollution prevention and capture, and validation of emissions to land, water, air and deposition on soil, would be necessary to improve confidence that these communities will no longer be exposed to excessive levels of hazardous RSCs.

Dioxins and furans

Dioxins and furans (“dioxins”) are among the most toxic chemicals that may be emitted from pulp mills. Their creation and release has been reduced as pulp mills have switched from elemental chlorine, to chlorine dioxide for bleaching. Dioxin levels are further reduced if oxygen is used in delignification, and peroxide is used later in the process. Sweden leads the world in advanced technologies for pulp manufacture.¹⁵

2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD), made famous as a contaminant of the defoliant Agent Orange used in the Vietnam War, is one of the most toxic, persistent, bioaccumulative man-made chemicals. This chemical is considered to be the most toxic, in the family of related dioxins and furans. With three chemical rings in a row, these are examples of poly-aromatic hydrocarbons (PAHs). Chlorinated PAHs have

chlorine atoms attached to the carbon structure. As a result of comparative toxicity based on historical experiences and scientific methods, dioxins and furans with four or more chlorine atoms (maximum eight chlorine atoms), including at the positions numbered 2, 3, 7 and 8, are considered extraordinarily toxic. Other dioxins are prorated in terms of toxicity, to calculate total toxic equivalents (TEQs).

An advance in pulp manufacture was made with introduction of chlorine dioxide bleaching that results in lower levels of chlorinated PAHs. Oxygen de-lignification, to which Northern Pulp committed during public consultation (see EA Registration document, Appendix 6), also assists to reduce use of chlorine based bleach and releases of chlorinated PAHs.

PAHs form, and may be chlorinated, during pulping and bleaching. PAHs can also form during combustion, and chlorination during combustion may be enhanced when the fuel contains higher levels of chlorine.¹⁶ This is expected to be the case with addition of sludge to feed the boiler. Temperatures also affect formation of PAHs.¹⁶ Thus, rigorous analyses of emissions and environmental contaminants are necessary to provide a baseline, as well as to monitor emissions and effects before and following operational changes in the pulp mill.

It is stated in the EA Registration document (e.g., Table 6.7-1), "In fact, dioxins and furans testing for the last 5 years has consistently shown that all of the compounds required to be tested under the regulations have not been detected in NPNS' effluent (non-detect)." The dioxin-free message is not consistent with reports from Northern Pulp that are posted on the Nova Scotia government website, nor the data reported to the National Pollutant Release Inventory (NPRI).¹⁷ NPRI data indicates that on average 3.6 tonnes of PAHs have been emitted to the air annually since 2006, and 8 mg TEQ dioxins/furans have been emitted annually since 2011.

Environment Australia published a helpful review of chlorinated dioxin and furan emissions.¹⁸ Of particular interest is a series of diagrams of typical dioxin "fingerprints" or patterns of emissions from various processes, as discussed below.

Biomass entering the pulp mill should contain little material with chlorine atoms bound to carbon atoms. In this case, typically there would be significant proportions of dioxins with four to six chlorine atoms (that have the highest TEQs), and lower proportions of dioxins with seven or eight chlorine atoms.

The opposite is reported for Northern Pulp in analyses reported on the Nova Scotia website, with all dioxin findings restricted to the hepta- and octo- (seven and eight) chlorinated forms. This is highly unusual. It is not consistent with the Australian experience,¹⁸ and is also not consistent with reports of changes in dioxin fingerprints in fish affected by emissions from a pulp mill on Lake Superior, after bleaching was switched from chlorine to chlorine dioxide.¹⁹

Although I know of no evidence of either of the following actually happening, I offer two possible explanations from my experience and research, for this unusual situation. There may be laboratory deficiencies and/or irregularities during analyses, or alternatively, wood chips treated with polychlorinated phenols (wood preservatives) may have been processed at the facility.^{18,20} These bear investigation.

In summary, regarding PAHs, including dioxins and furans:

- **Total chlorine free pulp production, with innovations to reduce water, waste and pollution, should be reassessed independently, because advanced technologies are established internationally. At a bare minimum, oxygen delignification must be installed as promised, to help to reduce toxicity of effluents, including both chlorinated PAHs (in particular dioxins and furans) and non-chlorinated PAHs;**
- **independent verification of laboratory analyses should be conducted, with blinded field blanks and, importantly, spiked samples included with field samples;**
- **possible origins of the unusual dioxin finger-print observed in samples from recent years should be investigated, including boiler fuels;**
- **the statement by Dillon, on behalf of Northern Pulp, that dioxins and furans have not been detected for the past five years is not true. This should be withdrawn. Releases of PAHs and other NPRI data should be reported.**

Looking for contaminants where they will be found, and pose hazards

While monitoring emissions directly is important for any industry, these samples do not adequately predict what is important – the levels of toxicants in the environment, and in foods and people. PAHs and metals emitted by NPNS are bioaccumulative. For example, lipophilic (“fat loving”) PAHs tend to bioaccumulate in fatty tissues,¹⁹ so analysis of aquatic organisms may reveal substantial levels despite “no detection” results in water or air. Similarly, metals attached to particulates may not be detected in finely filtered water or air, but may nevertheless build up in plants and animals. It is of course easier to measure pollutants when they are at higher concentrations, and is more relevant to the environment as well as to populations, to measure toxicants where they accrue and pose greatest hazards and risks.

According to a 2017 study of foods consumed by First Nations in the Atlantic Provinces, oysters and organ meat are highest in cadmium.²¹ Mussels²² and lobster hepatopancreas have been monitored for toxic chemicals in other situations (Appendix R of the Environmental Assessment). There are many options for relevant, sensitive longitudinal monitoring. It is beyond the scope of this work to offer recommendations, but it may also be time to expand toxicant and toxicity testing beyond simple acute fish mortality.

Summary

In summary, in my view, it is essential that the environmental assessment information for this project must include, at a minimum:

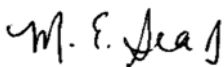
- independent scoping of a human health assessment, to ensure that the details and particulars of the diverse populations, vulnerabilities, changes in exposure within the particular contexts of these populations and their diets, and current industrial legacy pollution are adequately addressed;
- assessment of progressive measures to modernize equipment and processes in the mill, to eliminate pollutant exceedances, and to advance technologies and practices, to place NPNS as a leader in environmentally preferable pulp production, as well as promotion of public and environmental health;
- baseline and regular surveillance monitoring that is accurate, verified, reliable and relevant to the environment and human populations;
- investigation and assessment of any proposed developments, in recognition of legacy mercury contamination in proximity of the proposed effluent treatment facility;
- plans to minimize contamination and to monitor for contaminants and related effects, using both conventional measures as well as with assays of biological samples (e.g. shellfish).

Unfortunately, I could identify none of these in the current EA Registration package. What is more, inaccurate statements denying pollution that occurred cast a shadow over the reliability of the EA.

The above comments address a few, but given the time frame certainly not all, shortcomings and misperceptions within the Northern Pulp Environmental Assessment Registration documents. It is my opinion that the current EA Registration package is insufficient to permit adequate assessment, and that any permissions or approvals on this basis are not justified.

I hope that the above is of assistance, and am available for further discussions in this important matter.

Respectfully Submitted,



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APPENDIX F-2

Margaret (Meg) E. Sears (M.Eng., Ph.D.)

[REDACTED]

[REDACTED]

[REDACTED]

Capabilities and Experience:

Broad interests include health and medicine, epidemiology and toxicology, chemistry, ecology, biology and chemical engineering. Specific interests in ongoing work include environmental health, and scientific evidence synthesis for hazard and risk assessment, and public policy. A current focus is on multi-factorial contributors to chronic disease, and filling data gaps in environmental health epidemiology.

Activities include researching, assessing, reviewing and reporting in the scientific literature, for government bodies, peer-reviewed journals, and civil society organizations. My work includes liaising with a broad network of scientific experts, physicians and others on topics related to environment and health. I also frequently observe and participate in stakeholder meetings regarding the Chemicals Management Plan, and participate in federal government consultations and other meetings on chemicals management and pesticides. In 2015, two reports from the Parliamentary Standing Committee on Health included my recommendations regarding pesticides, and health effects of radiofrequency radiation. The *Canadian Environmental Protection Act* Parliamentary Committee and the *Canadian Environmental Assessment Act* Panel recommendations include some of my recommendations, and I participated with others and Canadian Environmental Law Association staff in drafting proposed amendments to the *Canadian Environmental Protection Act (1999)*. I have written key documents regarding environmental sensitivities and worked with groups of affected as well as health care professionals.

Experience includes working with groups of researchers on large scientific reports, including research question identification, literature searches, data extraction, analysis and review, writing, editing, managing references and maintaining version control. I chair the civil society organization *Prevent Cancer Now* and work with numerous other civil society organizations in Canada and internationally regarding toxic exposures. I have also twice been a medical journal guest editor. I have also conducted consultations among professionals, and citizens' groups, and prepared and presented scientific committee and tribunal submissions.

Public speaking includes lecturing at the Universities of Ottawa and Toronto, and Lakehead University, and numerous public presentations regarding topics in environmental health.

Topics recently addressed include hazard and risk assessment per federal legislation, and more specifically epidemiology, toxicology (including pesticides), endocrine disruptors, toxic elements, systematic review in environmental health, and electromagnetic radiation in public and personal health.

Diverse laboratory and field experience in chemical engineering, applied chemistry, and microbiology; including occupational health and safety, and microbiological and petrochemical industry research.

Academic Background

- 1986 Doctor of Philosophy, McGill University. Effects of growth conditions on biosorption by *Rhizopus* biosorbents.
- 1981 Masters of Chemical Engineering, McGill University. Measurement and mathematical modelling of biosorption of uranyl ion by biomass of the mould *Rhizopus arrhizus*.
- 1979 Bachelors of Applied Chemistry and Chemical Engineering, with Honours, University of Toronto.

Appointments

Senior Clinical Research Associate, presently working with Dr. Richard van der Jagt at the Environmental Health Information Infrastructure; previously under Dr. David Moher at the Centre for Practice-Changing Research, Epidemiology, at the Ottawa Hospital Research Institute

Associate with University of Sherbrooke, working with Dr. Isabelle Gaboury and colleagues

Previously Adjunct Investigator at the Children's Hospital of Eastern Ontario (this type of appointment was discontinued)

Professional Membership

Canadian Paediatric Society, including Environmental Health Section.
Canadian Public Health Association
Ontario Public Health Association
International Network for Epidemiology and Policy

Awards and Grants

- 2013 Carleton Lee Award, American Academy of Environmental Medicine
- 2007-2009 Canadian Institutes of Health Research / Social Sciences and Humanities Research Council grant for a scoping review on the toxic elements arsenic, cadmium, lead and mercury.
- 1980-1985 Natural Sciences and Engineering Research Council scholarship for post-graduate studies

Work Experience – University instruction

- 2012, 2014, 2017 University of Ottawa EVS 3131 (undergraduate) and Capstone Masters programs - Supervised and participated in student projects. Lectured on Environmental Health.
- 2010 – 2012 Lakehead University and the Northern School of Medicine - PUBL5213 Environmental and Occupational Public Health (Masters of Public Health). Lectured on toxicology and epidemiology, land use planning, evidence synthesis, pesticides, toxic metals and endocrine disruption, in a distance-learning course.
- 2011, 2012 Lectured on toxicology epidemiology and evidence synthesis, as well as pesticides, in ENV 341, at University of Toronto.
- 2009, 2010 Lectured on toxicology, epidemiology, evidence synthesis, pesticides and toxic metals in HSS3303 at the University of Ottawa.

Work Experience - selected

- 2018 Preparation of an Indoor Air Quality Module regarding Chemical Sensitivities, for the Canadian National Research Council.
- 2013-2014 – Health expert in the Proceeding of the Alberta Energy Regulator re. health effects of bitumen emissions in the Peace River area.
- 2012 Health expert in Fortis BC hearing re. Smart Meters
- 2004-on Systematic Reviews in the Centre for Practice Changing Research at the Ottawa Hospital Research Institute, under Dr. David Moher. Many aspects of evidence review and synthesis, and editorial responsibility for large medical scientific research reports.
- 2003-on Work with diverse medical researchers, on data analysis, presentation and writing, in Ottawa, Toronto and at the University of Sherbrooke.
- 2011 In conjunction with physicians associated with the Ontario College of Family Physicians, I conducted literature searches, synthesis of information and co-writing of a report regarding updating the Greig Record for child and adolescent primary care visits with Family Physicians.
- I organized and spoke at a meeting to present Toxic Metals in Canadians scoping review findings and to gain insights from physicians, clinical and toxicological researchers, and public health officials.
- 2009 Co-authored “Air Travel and Chemical Sensitivities” for the Canadian Transportation Authority.
- 2008 Canadian Institutes of Health Research Primary Investigator - “Toxic Metals in Canadians and their Environments: Exposures, health effects, and physician and public health management strategies - A Scoping Review”
- 2008-on Occasionally assist the David Suzuki Foundation with scientific review of documents regarding environmental health topics, including pesticides and cosmetics.
- Prepared affidavits with regard to health effects of herbicides (and contaminants) used at CFB Gagetown, NB.
- Lectured on epidemiology, toxicology and synthesis of scientific evidence in environmental health, pesticides, toxic elements (particularly arsenic, cadmium, lead and mercury) as well as scientific writing, in undergraduate courses at the University of Ottawa and University of Toronto, and at the graduate level (Masters of Public Health) at Lakehead University.
- 2006 Prepared “A Medical Perspective on Environmental Sensitivities” for the Canadian Human Rights Commission, including research review, and consultation with physicians, architects and civil society organizations.
- 2002-on Writing, and assisting medical researchers and others with drafting of research documents.
- This work includes data extraction, review of data and statistics, review of the medical background information, literature review updates, and planning, drafting and version control.
 - Articles have included systematic reviews, randomized controlled trials, other interventional and observational studies, and commentaries.
 - Topics include pesticide assessment and 2,4-D, environmental sensitivities, medical ethics, medical education, diabetes in children, probiotics, sexuality and fertility

following spinal cord injury, breast cancer care, child car-seats and booster-seats, nocturnal enuresis, omega-3 fatty acids and infant health, computerized physician order-entry systems in the context of bronchiolitis, childhood arthritis, models of medical practice and collaboration, lipid modifying agents, drug delivery, TPMT assessment in thiopurine therapy, morphine monitoring nursing practice, nutritional supplements and drugs for cardiovascular health, and online medical education.

2002 Drafted “Frequently Asked Questions” responses regarding breast milk contamination, flame retardants, West Nile virus and insect repellents, for the Canadian Institute of Child Health.

1979-80 Research engineer at Gulf Canada's research facility in Sheridan Pk., Mississauga. Constructed and operated small-scale laboratory simulation of heavy oil cracking, as well as mathematical modelling of enhanced oil recovery (akin to 4-phase hydrogeology).

1975-79 During summers prior to and during undergraduate studies, worked in UofT Chemical Engineering laboratories (including tar sands oil extraction), and at Imperial Oil Research laboratories.

Volunteer Activities

2017 Member of the Science Committee for the Canadian Public Health Association 2018 Conference Planning Committee

2017 Core leadership group and 2018 Conference planning for the Canadian Alliance for Regional Risk Factor Surveillance

2015-on member of Waste Watch Ottawa, that brings strong evidence regarding waste management to Ottawa City Council

2011- on Board member (currently Chair) of *Prevent Cancer Now* (www.preventcancer.ca). Responsible for writing and editing publicly available documents, media, and numerous public presentations regarding cancer prevention.

With Dr. van der Jagt, initiating a national environmental health information infrastructure for investigation of links between environmental quality and health.

2011- on Member of the Sustainability Committee (“Green Team”) at the Children’s Hospital of Eastern Ontario, Ottawa.

2001- on Established, along with other mothers, the Ottawa Neuroblastoma Research Fund (CHEO)

2001- on Work with physicians and various organizations regarding pesticides and health.

2002- on (currently quiescent) Founding member of the Coalition for a Healthy Ottawa and the Canadian Coalition for Health and the Environment. We synthesized and promoted research on pesticides and health, as well as synthesis of scientific evidence, in efforts to reduce use of pesticides in urban areas, and for vector control, with these and other groups across Canada.

1995-8 Member of the Board of Directors of *Les Petits Ballets*, in charge of publicity.

1989-on (currently quiescent) Founding member and Secretary for the Wetlands Preservation Group of West Carleton, working for environmental protection before the Ontario Municipal Board, Environmental Assessment Advisory Committee, in court, and before the Sewell Commission on land use planning.

Peer-reviewed publications

Fernández, C., A. A. de Salles, M. E. Sears, R. D. Morris, and D. L. Davis. "Absorption of Wireless Radiation in the Child versus Adult Brain and Eye from Cell Phone Conversation or Virtual Reality." *Environmental Research*, June 5, 2018. <https://doi.org/10.1016/j.envres.2018.05.013>.

Sears, Margaret E. Chelation: Harnessing and Enhancing Heavy Metal Detoxification: A Review. *The Scientific World Journal* 2013 (April 18, 2013). doi:10.1155/2013/219840.

Kanji, Salmaan, Dugald Seely, Fatemeh Yazdi, Jennifer Tetzlaff, Kavita Singh, Alexander Tsertsvadze, Andrea C. Tricco, et al. "Interactions of Commonly Used Dietary Supplements with Cardiovascular Drugs: a Systematic Review." *Systematic Reviews* 1, no. 1 (May 31, 2012): 26.

Seely D, Kanji S, Yazdi F, Tetzlaff J, Singh K, Tsertsvadze A, Sears ME, Tricco A, Ooi TC, Turek M, Tsouros S, Skidmore B, Daniel R, Ansari MT. Dietary Supplements in Adults Taking Cardiovascular Drugs. Comparative Effectiveness Review No. 51. (Prepared by the University of Ottawa Evidence-based Practice Center under Contract No. HHSA 290-2007- 10059-I.) AHRQ Publication No. 12-EHC021-EF. Rockville, MD: Agency for Healthcare Research and Quality. April 2012.

Sears, Margaret E., Kathleen J. Kerr, and Riina I. Bray. Arsenic, Cadmium, Lead, and Mercury in Sweat: A Systematic Review. *J Environ Public Health*. Article ID 184745 (2012): 1–10.

Sears, Margaret E., and Stephen J. Genuis. Environmental Determinants of Chronic Disease and Medical Approaches: Recognition, Avoidance, Supportive Therapy, and Detoxification. *J Environ Public Health*. Article ID 356798 (2012): 1–15.

Loit E, Tricco AC, Tsouros S, Sears M, Ansari MT, Booth RA. Pre-analytic and analytic sources of variations in thiopurine methyltransferase activity measurement in patients prescribed thiopurine-based drugs: A systematic review. *Clin Biochem* (March 18, 2011). 44(10-11):751-757.

Sears M. Toxic Metals Injuries. *Paed Child Health*. 2011;16(3):152.

Sharma M, Ansari MT, Soares-Weiser K, Abou-setta AM, Ooi TC, Sears M, Yazdi F, Tsertsvadze A, Moher D. Systematic review: comparative effectiveness and harms of combination therapy and monotherapy for dyslipidemia. *Annals of Internal Medicine* 151, no. 9 (November 3, 2009): 622-630.

Sharma M, Ansari MT, Soares-Weiser K, Abou-setta AM, Ooi TC, Sears M, Yazdi F, Tsertsvadze A, Moher D. Comparative Effectiveness of Lipid-Modifying Agents [Internet]. Rockville (MD): Agency for Healthcare Research and Quality (US); 2009 Sep.

Sears M and Walker CR. Dioxins in Children. *Paediatric and Perinatal Drug Therapy*, 2007; 8 (3):134.

Sears M, Walker CR, van der Jagt RHC, Claman P. Pesticide assessment: Protecting public health on the home turf. *Paediatr Child Health* 2006;11(4):229-234.

Irwin D, Vaillancourt R, Dalgleish D, Thomas M, Grenier S, Wong E, Wright M, Sears M, Doherty D, Gaboury I. Standard concentrations of high alert drug infusions across paediatric acute care. *Paed. Child Health* 2008;13(5):371-376.

Treen-Sears ME, Volesky B, Neufeld RJ. Ion exchange/complexation of the uranyl ion by *Rhizopus* biosorbent. *Biotechnol. Bioeng.* 1984;26(11):1323–1329.

Treen-Sears ME, Martin SM, Volesky B. Propagation of *Rhizopus javanicus* Biosorbent. *Appl Environ Microbiol.* 1984; 48(1):137–141.

Treen-Sears ME, Martin SM, Volesky B. Control of Rhizopus Biosorbents' Quality During Propagation. *Fundamentals of Applied Biohydrometallurgy*; Vancouver, BC; Canada; 21-24 Aug. 1985. pp. 305-308.

Volesky B, Sears M, Neufeld RJ, Tsezos M. Recovery of strategic elements by biosorption. *Annal NY Acad Sci* 1983.

Nadeau JS, Treen ME, Boocock DGB. Mass transfer effects in a nitric oxide dosimeter. *Anal. Chem.* 1978;50(13):1871-1873.

Guest Editor: *Journal of Environmental and Public Health*. Special issue on Incorporating Environmental Health into Clinical Medicine, published spring of 2012.

Guest Editor: *The Scientific World Journal*, Special issue on Environmental Health, published spring 2013

Peer Reviewer: Canadian Medical Association Journal; European Journal of Internal Medicine; Reproductive Toxicology; Journal of Forensic Sciences; Paediatrics and Child Health; Human and Experimental Toxicology; Public Health; Science of the Total Environment; International Journal of Environmental Research and Public Health; Current Oncology.

Book Chapter

Davis, D, M Sears, A Miller, R Bray. Microwave/Radiofrequency Radiation and Human Health. In *Integrative Environmental Medicine*. A Cohen, FS vom Saal Eds. Oxford University Press. March 2017.

Recent Conference Participation

2018 Core organizing committee for CARRFS pre-conference session, and speaker (**Escalating Chronic Disease in Young Canadians – surveillance for environmental links**) at the collaboration session during the Canadian Public Health Association conference, Montreal.

2017 Presentations and participation in an experts forum at The Hebrew University, hosted by the Israeli Institute for Advanced Studies, and the Environmental Health Trust. "**Wireless Radiation and Human Health.**" Jerusalem, January 2017.

2015 "**Scientific Review to Support Public Policy Regarding Exposure to Radiation from Wireless Communications Devices.**" Poster. International Bioelectromagnetics Conference. Alisomar, California. June 2015

2014 "**Search and ye shall find environmental health concerns: e.g. Peace River Proceeding1769924.**" Invited Presentation. Under Western Skies Conference. Calgary. September 2014.

2013 "**Harvesting the Best from the Wilderness: Moving from Scouts' Common Sense, to Evidence-Based Practice for Environmental Health.**" Invited presentation. American Academy of Environmental Medicine. Phoenix, Arizona

Selected non-peer reviewed medical / scientific articles

Ongoing, submissions regarding policy and laws improvements, and scientific comments regarding substances and exposures to the Government of Canada and others, on behalf of Prevent Cancer Now. <http://www.preventcancer.ca/main/resources/cancer-prevention-submissions>

Healthy Children/Healthy Environment: Improving the Odds: Part 2

(authors in alphabetical order) Riina I. Bray, M. Janet Kasperski, Lynn M. Marshall, Margaret E. Sears.

[March 31, 2011. Respectfully submitted on behalf of the Ontario College of Family Physicians to the Environmental Health Program, Health Canada.]

Air Travel and Chemical Sensitivities

John Molot, Lynn Marshall and Meg Sears

[March 2009 – prepared for the Canadian Transportation Authority]

The Medical Perspective on Environmental Sensitivities

Margaret E. Sears [February 2007 – prepared for the Canadian Human Rights Commission, in collaboration with the Ontario College of Family Physicians Environmental Health Committee, and other academics, physicians and architects]

Available at: <http://www.chrc-ccdp.gc.ca/eng/content/medical-perspective-environmental-sensitivities>

Comments on the Pest Management Regulatory Agency’s Use of Uncertainty and Safety Factors in the Human Health Risk Assessment of Pesticides

M.E. Sears, C.S. Findlay, N. Arya, L. Marshall, M. Sanborn, K.J. Kerr, J. Kasperski

[2007 – prepared on behalf of, and submitted to the Pest Management Regulatory Agency (PMRA) of Health Canada, by the Environmental Health Committee, Ontario College of Family Physicians]

APPENDIX F-3

Chapter 4

The Greening of the Pulp and Paper Industry: Sweden in Comparative Perspective



Ann-Kristin Bergquist and Kristina Söderholm

4.1 Introduction

Since the 1960s, concern about environmental degradation has greatly altered the commercial conditions for most industries in the Western world, but the global pulp and paper industry (PPI) has encountered more serious challenges than most other industries. The reason is that pulp and paper production, especially bleached pulp manufacturing, is extremely damaging to the environment. Thus, pulp mills cause, among other things, emissions of odorous gases and sulphur compounds into the air and of organic and inorganic chemicals including chlorinated compounds and other substances into waterways. Thanks to technological developments, however, the environmental situation has been greatly improved during the last five decades with reduced emissions; in many cases the reduction has been more than 90%. This chapter concerns the environmentally driven transformation of the PPI and examines it in a country which has pioneered parts of the greening process in this industry, namely Sweden. This nation is one of the world's leading pulp and paper countries, as it ranks as the ninth largest producer of paper and the fourth largest producer of pulp (Lamberg et al. 2012; Järvinen et al. 2012; Bergquist and Keskitalo 2016).

For any polluting industry, technology is at the very core of the challenge to reduce its environmental impact (Jaffe et al. 2005) and indeed this has been the case for the PPI (Bajpai 2011). Technological strategies and timing for investments have differed between countries and regions depending on the different national jurisdictions, organizational solutions, demand characteristics and geographical circumstances. The

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literature on corporate environmentalism, which has stressed companies' modes of responding to environmental issues, has generally identified a movement along an evolutionary, adaptive learning process that formed specific attitudes or means of response during certain periods (Hoffman and Bansal 2012). An important conclusion from this research when it comes to technological strategies is that before the 1990s, firms typically employed end-of-pipe approaches to achieve regulatory compliance, which practically means external treatment of effluents after they have left the plant (Lee and Rhee 2005; Frondel et al. 2007; Hoffman 1997). The alternative technological approach, internal process changes (e.g., in-plant measures that prevent or reduce effluents before they leave the plant, sometimes also referred to as 'cleaner production technologies'), has subsequently been acknowledged and adopted as a more advantageous and effective strategy (Sinclair 1990).

As will be discussed in this chapter, Swedish PPI has not followed the textbook example of the learning process from end-of-pipe technology to "cleaner" production processes. The Swedish PPI, in contrast to both its North American and Finnish counterparts, embarked already in the 1970s on developing internal process alterations rather than end-of-pipe solutions, as the main technological strategy for pollution control (Bergquist and Söderholm 2015; Harrison 2002). This early strategy became formative for the Swedish PPI's green technological development for decades to come. Kemp and Soete (1990) have argued that, compared to 'normal' technological efforts in industry, pollution control efforts are generally more focused on incremental improvements in 'cleaning' technology, following relatively well-established technological strategies of 'progress'. This argument suggests that pollution control technologies are particularly 'path dependent' and breaking the 'path' demands a lot of investments and even a new way of thinking. The notion of path dependence can be seen from several perspectives; from the simple assertion that 'history matters' to the problem of imperfect information and the appreciation that institutional arrangements may have limits, and the phenomenon of increasing returns (e.g. Liebowitz and Margolis 1995; Pierson 2000). When it comes to technology, path dependence can provide very powerful incentives for limiting actions to incremental technological solutions, which in turn strengthen established lines of action (Geels 2004; Kemp and Soete 1990; David 1994). Technological approaches in one country, as well as divergent technological strategies between different pulp and paper producing countries, might therefore be considered in the logic of technological path dependence.

For several reasons the greening of the PPI has been a core challenge for the sector. Environmental regulations have greatly altered the commercial conditions for the PPI over the past five decades (as for most industries), and since the 1980s, market pressure has also interacted with environmental regulation as a driver towards greener production processes and products. In addition, since the 1970s, the drive to use energy more efficiently has been increasingly linked with environmental issues, not least through the issue of climate change. Overall, the greening of the PPI has been a complex process. It has evolved along several different paths in combination with other business challenges, with the latter stemming from changed input

prices on, for instance, energy, wood and labour and also changes in market competition, governmental policies, and new technologies outside the immediate realm of pollution control.

4.2 Environmental Impacts of Pulp and Paper Production: A Short Background

The environmental impact of pulp and paper mills has been, and still is, serious from many aspects (Table 4.1). It causes or produces human toxicity, ecotoxicity, photochemical oxidations, acidification, nitrification, solid wastes and climate change (Bajpai 2011). Still, the situation is much better today than it was in the past; wastewater from a modern pulp mill contains only a small fraction of the contaminants that it did in the 1960s. One of the most serious problems is the very large quantity of wastewater resulting from pulp manufacturing, and it is contaminated with a number of organic and inorganic chemicals including lignin, cellulosic compounds, phenols, mercaptans, sulphides and chlorinated compounds (Thompson et al. 2001). The PPI is also a large user of both energy and water, and toxic chemicals. For example, in the United States (US) the paper industry is the third largest energy user among manufacturing industries, accounting for 11% of domestic energy consumption in 2010 (World Watch Institute 2015). The most significant environmental problems occur in the stage of the pulping process (in relation to paper production), which is why the most severe problems in the past were found in pulp producing countries, such as Sweden, Finland, Canada and the US although pulp importing countries, such as the United Kingdom and Germany also have struggled with severe problems (Bajpai 2015; Bergquist and Söderholm 2015; Mutz 2009).

Pulp can be roughly divided into the processes (and products) of mechanical and chemical pulp. Each process varies in terms of immediate environmental impact depending upon the amount and type of energy and chemicals used. Pulp mills are, however, traditionally associated specifically with the discharge of high levels of wastewater contaminated with organic matter. In the chemical pulp process, wood chips are first cooked in chemicals and then the solution is washed to produce “clean pulp”, which consists of only cellulose fibres. Dirty “wash water”, containing cooking chemicals and dissolved lignin, are thereafter sent to a recovery boiler¹ from which the cooking chemicals are recovered for reuse and the lignin is burned for power generation. Wastewater containing the remaining organic matter and chemicals is then discharged (Gunningham et al. 2003, pp. 10–11).

The most serious environmental problem related to pulp manufacturing in the past was caused by the bleaching process. It takes place in stages, generally alternating between acid and alkaline stages. The use of elemental chlorine (Cl₂) as the bleaching agent became dominant in the 1950s (Norberg-Boom and Rossi 1998) and was

¹The invention of the recovery boiler by G. H. Tomlinson in the early 1930s was a milestone in the advancement of the Kraft pulp process.

Table 4.1 Major pollution problems caused by pulp and paper production

Suspended solids (SS)	Have its origins in bark, pieces of fibres and filling, and coating agents. Consumes oxygen when decaying and can be carriers of poisonous substances
Organic matter in general (BOD and COD)	Uses oxygen from water. May cause oxygen deficiency in waterways, which leads to the death of, i.e., fish and cause severe damage to the ecosystem
Chlorinated organic compounds (AOX)	From mills using elemental chlorine in their bleaching sequence. Wastewater containing organic matter formed by elemental chlorine reacting with wood products to form absorbable organic halide (AOX). AOX has become an accepted measure of chlorinated organic material, and is used to monitor and regulate bleached Kraft pulp mill effluents. AOX is used as a surrogate parameter of dioxins in wastewater (and stack gas) from pulp mills
Water consumption	Pulp mills are major water users. Consumption of fresh water can seriously harm habitats near mills from reduced water levels (necessary for fish) and changed water temperature (also a critical environmental factor for fish)
Sulphur dioxide (SO ₂) and reduced sulfur compounds	Leads to acid rain and causes soil degeneration
Nitrogen oxides (NO _x)	Gases composed of nitrogen and oxygen formed during combustion. In moist air, the substances are converted into nitrogen oxides and then nitric acid, which creates acid rain. Originates from recovery boilers in the Kraft pulp process
Sulphur compounds (TRS gases)	Smell

Source Ince et al. (2011), Skogsindustrierna (1995), Nilsson (2007)

subsequently replaced after the 1980s with new bleaching agents and methods such as the elemental chlorine free (ECF) and total chlorine free (TCF) bleaching.

4.3 Environmental Regulation as a Driver for Technology Development

The Swedish PPI has been central to the Swedish economy ever since the introduction of mechanical pulp in the 1850s and chemical pulp in the 1870s. Already at the time of the First World War Sweden was the world's second largest pulp producer after the US and the world's largest pulp exporter (Fahlström 1948; Rydberg 1990; Järvinen et al. 2012). As the PPI represented both one of the largest industrial sectors in Sweden and one of the biggest polluters, it has received much attention in Swedish policy to control industrial pollution, including joint state-industry efforts in R&D to control it (Bergquist and Söderholm 2011).

Over time environmental policies have grown more complex with a long-term shift in focus from local conflicts over water pollution and odour problems in the late nineteenth century to transnational and global problems such as climate change in the late twentieth century. This development has taken place in stages (McNeill 2000). Hence, in the 1960s, Sweden along with many other western societies saw the initiation of serious governmental action to control industrial pollution in parallel to a growing environmental awareness in society (Lönnroth 2010). In contrast to the US, environmental awareness in Sweden grew mainly amongst experts and not the public in the 1960s and 1970s. It is often assumed that heavy polluting industries did not focus seriously on mitigating their environmental impacts before this environmental awakening. There is plenty of historical research, however, which illustrates how companies and even industrial sectors undertook action to control pollution due to local conflicts and governmental intervention before the 1960s and sometimes they did so even proactively to avoid a bad outcome for business (for an updated literature overview, see Bergquist 2017). In fact, the Swedish PPI undertook action to control pollution long before the 1960s due to increasing local criticism and the industry's own awareness of the negative environmental effects from production. This in turn spurred joint efforts to develop new and cleaner technologies already in the early 1900s (Söderholm and Bergquist 2012). For example, by 1908 all Swedish sulphate pulp producers had united to form the so-called *Sulphate Pulp Committee* to develop technology to lessen the odour problem stemming from the sulphate pulp process.² Central reasons behind these initiatives were rising concerns about industrial pollution that had been expressed in the Swedish Parliament in the early 1900s, along with court cases concerning the contaminating activities of single pulp mills. These court cases built on early health- and water protective regulation, which to some degree included regulation of industrial pollution. For instance, the Public Health Act of 1874 constituted the first governmental “all-embracing” attempt to address sanitary issues. In the 1910s, the Swedish government presented a proposal to implement stricter legislation against air and water pollution. However, the proposal was rejected in the early 1920s due to an economic recession (Söderholm 2009; Lundgren 1974).

Pollution problems, however, increased in tandem with a growing Swedish economy in the 1930s, whereupon the Swedish government initiated a process of tightening the regulation of water pollution. Hence the Water Act was reformed in 1942, whereby it introduced a concession system according to which enterprises such as chemical pulp and sugar mills and textile factories had to apply to the Water Court for permission to operate. Still, air pollution was not addressed properly until 1963, and then through the formation of the State Air Pollution Control Board (Lundgren 1999). Finally, in 1969, the Environmental Protection Act (EPAAct), the first uniform Swedish framework for regulating air and water pollution, noise and other disturbing activities from industrial plants, was passed by the Swedish Parliament. Years before the final bill was enacted, the construction of a modern system for environmental

²For a more detailed overview of regulation and organization of the Swedish PPI during this period, see Söderholm and Bergquist (2012).

protection had begun in Sweden. Thus, in 1967 the government created the National Environmental Protection Agency (EPA), a unified body for almost the entire area covered by the Environmental Protection Act (Lundqvist 1971). Soon other countries followed this lead, such as the US, which established its own EPA in 1970. Still, in the neighbouring pulp producing country of Finland, environmental policy developed at a slower pace (Söderholm et al. 2017). The National Board of Waters was created in 1970, but it was not until 1983 that a unified body to handle a major part of the environmental issues founded there (i.e., the Ministry of the Environment) (Joas 1997).

From the 1970s until the 1990s, the Swedish EPA was the main tool to control pollution and other environmental problems related to Swedish industry, and it fundamentally changed the conditions for the operations of the Swedish PPI. Thus, in the 1970s and the 1980s it forced the sector to increase considerably its green R&D activities and to undertake deep emission cuts (Bergquist and Söderholm 2011). The regulatory approach was based on case-by-case assessments whereby permits had to be reassessed and renewed every 10 years or after production increased. It relied on so-called performance standards rather than technology standards and these were negotiated with each plant owner, sometimes over extended periods of time. The standards were typically implemented in combination with extended compliance periods, meaning that the companies were giving necessary time to develop and test technology. In these ways, the regulatory approach provided scope for environmental innovation and permitted the affected companies to coordinate pollution abatement measures with productive investments (Bergquist et al. 2013). In 1999, the EPA along with 15 other acts were amalgamated into the Swedish Environmental Code and the responsibility for issuing permits was thereby transferred from the Franchise Board of Environmental Protection (the organ responsible for issuing permits since 1969) to the Environmental Courts (Michanek and Zetterberg 2007).

The Swedish PPI has also been governed by European Union (EU) environmental legislation ever since Sweden became an EU-member in 1995. One example is the Integrated Pollution Prevention Control Directive (IPPC Directive) of 1996 and 2008. The IPPC Directive is a key instrument in the EU's environmental legislation, and its purpose is to achieve 'integrated pollution prevention' and control of the pollution occurring at large industrial installations (Schoenberger 2009).³ Further, in 2011, the Industrial Emission Directive (IED)⁴ came into force, meaning all Member States before 7 January 2013, had to incorporate the IED into national leg-

³The conditions of required permits have to be based on Best Available Techniques (BAT), and in 1997, the Sevilla Process was established to develop BAT. Since then, 33 BAT Reference Documents (BREFs) have been drafted, adopted and published containing ambitious consumption and emission levels which cannot be found anywhere else (Schoenberger 2009).

⁴The IED is the successor of the IPPC Directive and, in essence, is about minimizing pollution from various industrial sources throughout the EU. Operators of industrial installations are covered by Annex I of the IED and are required to obtain an integrated permit from the relevant EU country authorities. Permit conditions including emission limit values (ELVs) must be based on the Best Available Techniques (BAT) as defined in the IPPC Directive.

isolation. In Sweden the directive was included in the Industrial Emission Regulation (*Industriutsläppsförordning* 2013, p. 250) (SEPA 2016).

Since the 1990s in Sweden, policies targeting the PPI sector have embraced a blend of mandatory governmental and voluntary stipulations concerning social and environmental requirements. Thus, in line with international trends, environmental management systems (EMAS) have been implemented in virtually all Swedish pulp and paper mills. And most mills have chosen to certify their environmental management systems under either the global standard ISO 14001 and/or the European EMAS scheme. Thus, in 2013, 97% of the pulp and 98% of the paper produced in Sweden was manufactured under certified environmental management systems (Swedish Forest Industry Federation 2015). Essentially the EMAS scheme is an opportunity for producers to formally demonstrate from year to year their improved environmental performance to customers and partners, and is thus a form of ‘eco-labelling’. The opportunity for the Swedish PPI to engage in ‘eco-labeling’ first appeared in the 1980s (see below). Regulatory measures to stimulate improvements in energy efficiency and lower carbon dioxide emissions have developed as an additional control box parallel to other emissions (see e.g. Thollander and Ottosson 2008; Henriksson et al. 2012). Also, in 2005 the voluntary Swedish Program for Energy Saving (PFE) came into force (Henriksson et al. 2012).

4.4 The “Spring-Cleaning” of the Swedish PPI

4.4.1 *Internal Process Changes and Structural Rationalizations*

The magnitude of pollution control implied by the EPA Act in 1969 made the Swedish pulp and paper producers conclude that it was only through reconstructed and new plants embodying the most novel techniques that the discharges could be substantially reduced and requirements met (Wohlfart 1971b, p. 320). In this context, the Swedish pulp producers strategically aimed for production expansion based on the adoption of the sulphate process in the late 1960s, since the calcium-based sulphite mills had many environmental disadvantages in terms of their discharges of BOD, lignin, gases and dust, and chemical recovery. The discharges of the sulphite mills required radical external purification works while the sulphate process had the potential to recover chemicals and at the same time generate electricity (Wohlfart 1971b). Thus, the enforcement of the EPA Act made it economically impossible for some mills to continue operating, especially small, inefficient mills, many of which were forced to shut down. And it was in this context that Swedish sulphite pulp mills were almost totally phased out. The Domsjö sulphite mill owned by the MODO Group is, however, one of few sulphite mills that survived in Sweden after the 1970s (Söderholm and Bergquist 2013).

Contributing to the reduction of discharges from the PPI was a process of structural rationalization, and Sweden was not the only country to experience this phenomenon. The OECD stated in 1973 that replacing small, uneconomical and environmentally obsolete units with larger more energy- and resource-efficient mills would create cost-effective means of reducing discharges per production ratio opportunity without deviating from the business inclination to seek productivity gains through capacity expansion. The approaches, however, differed between countries. In most cases, oxygen depletion of waterways required the rapid adoption of stringent Biochemical Oxygen Demand (BOD) limits, which typically locked industry into end-of-pipe measures (Rajotte 2003; OECD 1973). In Sweden, however, the pulp and paper producers at the time of the enforcement of the EPAct had a basic approach developed, one that already defined decades of environmental development activities and which they aimed at maintaining (i.e., to cope with the pollutants inside the mills and not when they “leave the plant”) (Wohlfart 1971a, pp. 432–434).

The Swedish PPI’s approach to dealing with pollution through changing internal processes can be traced back to the 1940s and 1950s and the pioneering R&D activities then taking place within collaborative platforms established jointly by the industry sector (see Sect. 4.4.3 below). While the first collaborative initiatives of the sector to deal with pollution problems had taken place already at the turn of the twentieth century, the R&D activities thereafter increased in tandem with the development of environmental policy up to the 1960s. During this novel period, attention was foremost directed towards improved efficiency and reduced fiber emissions. The practice of discharging fibers was highly inefficient as it resulted in 15% waste. Increased efficiency was therefore closely linked to the ability to reduce discharges of organic materials (Söderholm and Bergquist 2012). Also Swedish authorities and other industrial sectors, such as the metal smelting industry, early on chose to focus on in-plant measures and primary effluents instead of external measures (Lindmark and Bergquist 2008). For example, in describing this strategy, the environmental manager of Stora Enso in the 1990s explained that ‘internal process changes have a completely different potential for the business. An end-of-pipe is a cost. An integrated solution can provide so much more. It can provide opportunities to increase production, reduce operating costs, and simply increase productivity. The key to all the improvements we have seen over the years is that the industry has been able to expand. The basic rule is that environmental improvements are a consequence of the corporate will to invest and its propensity to do so in the future. You take care of environmental costs as an integrated part.’⁵

4.4.2 *Emission Reductions and Costs*

During the 1970s and 1980s, costs for environmental investments were considerable for the Swedish PPI and accounted for 9–14% of the total investments (see Table 4.2).

⁵Interview with Per G Broman, Falun, 9 May 2006.

Table 4.2 Environmental investments in the Swedish pulp and paper industry, 1968–1988. Real prices (2000) million SEK (deflated using investment price index for the pulp and paper industry)

	68–70	71–75	76–79	80–84	85–88	Total
Environmental investments	930.2	4254.7	2372.9	2235.1	3388.9	13101.5
Environmental investments (share of total investments)	6	12.15	13.67	9.9	13.5	na

Source Swedish Forest Industries' Water and Air Pollution Research Foundation (SSVL) 'SSVL 74–85' (1989), see *Miljöskyddskostnader inom Svensk Skogsindustri 1985 t o m 1991. Appendix 2 and 20*. The estimates are based on questionnaire data collected by SSVL during the periods 1968–1970, 1971–1975, 1976–1979, 1980–1984, and 1985–1988. For a detailed accounting, see Söderholm and Bergquist (2012)

Over 60% of these investment costs involved altering internal processes that aimed to decrease water use and improve chemical and fibre recycling while about 14% of the costs concerned external wastewater purification measures. The cost share for air-purification measures amounted to only 15% (SSVL 1991, p. 93).

Costs were the highest among pulp producers (in comparison to paper producers), a sector in which the share of environmental investments in 1985–1988 accounted for as much as 17.5% of total investments (SSVL 1989, Appendix 10). This share was even higher among producers of bleached pulp at the beginning of the 1990s due to the discovery in the mid-1980s of the formation of dioxin in the process of pulp bleaching. Reported expenditures of US mills during the 1970s were on average 24% (i.e., higher than for the Swedish mills). However, during the 1980s capital expenditures on pollution control in the US PPI declined to 8.1% (Smith 1997, pp. 109ff).

The environmental investments undertaken by Swedish pulp and paper producers generated significant emission cuts. One example occurred in terms of Chemical Oxygen Demand (COD), which over the period 1970–1995 decreased from approximately 2.3 to 0.4 million tons annually. Moreover, from the mid-1980s to 2010 emissions of absorbable organic halides (AOX) declined by 97%.⁶ AOX is associated with dioxin and is a measure of total halogens (chlorine, bromine, iodine). Emissions of sulphur, AOX and COD are shown in Figs. 4.1, 4.2 and 4.3, while pulp production is shown in Fig. 4.4.

⁶<http://www.skogsindustrierna.se/skogsindustrin/branschstatistik/hallbarhet/>. Accessed 19 January 2018.

4.4.3 Firm Collaboration

A central part of the technologies that generated the significant emission cuts illustrated in Figs. 4.1, 4.2, 4.3 and 4.4 were developed within collaborative R&D arenas of the Swedish PPI. And at the time of the enforcement of the EPAAct (1969) these measures were supported by environmental authorities and involved various actors of importance to the innovation process. Two new collaborative environmental R&D

Fig. 4.1 Emissions of sulphur 1970–2014 (tons).
Source Skogsindustriernas miljödatabas

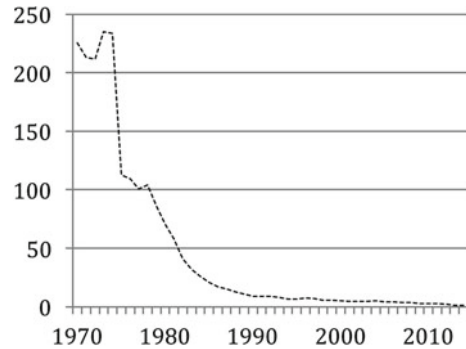


Fig. 4.2 Emissions of AOX 1978–2014 (tons). Source Skogsindustriernas miljödatabas

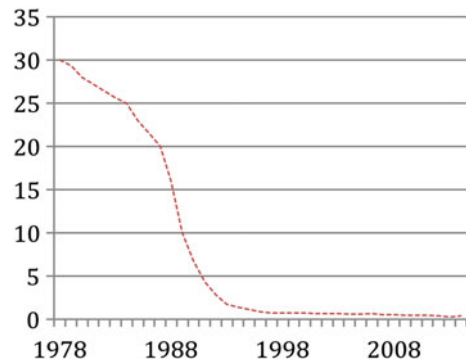
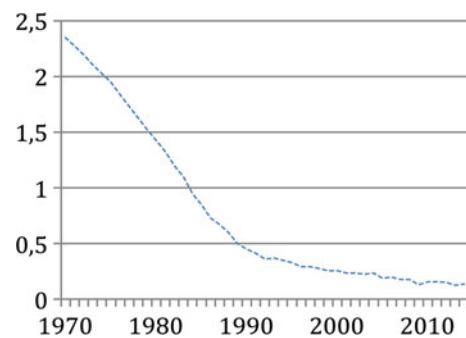


Fig. 4.3 Emissions of COD 1970–2014 (million tons). Source Skogsindustriernas miljödatabas



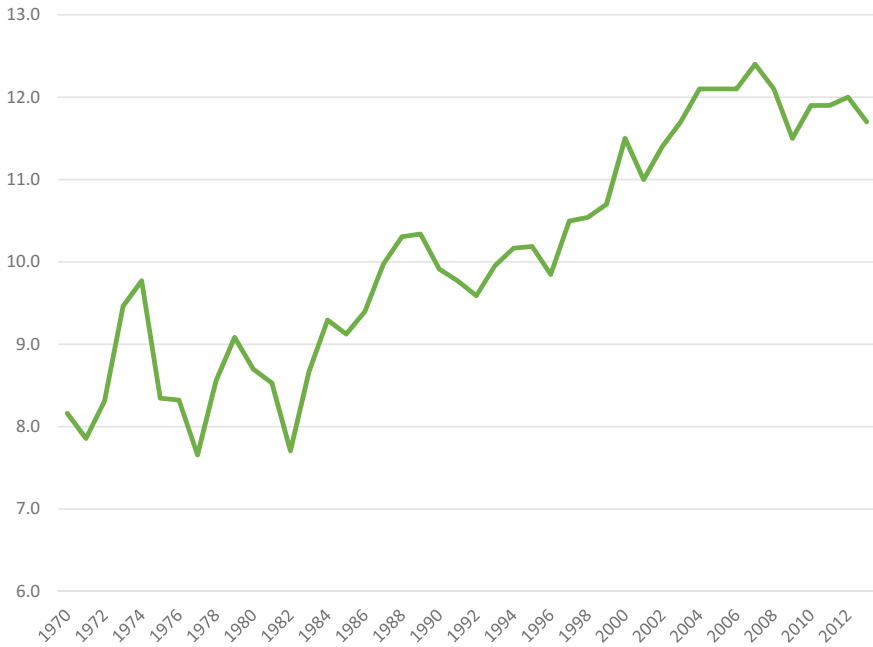


Fig. 4.4 Swedish pulp production 1970–2013 (million tons). *Source* Skogsindustriernas miljö-databas

platforms were established by the Swedish PPI in the 1960s. These were the state- and industry-funded Institute for Water and Air Protection (IVL), created in 1966, and the Forest Industries’ Water and Air Pollution Research Foundation (Stiftelsen Skogsindustriernas Vatten- och Luftvårdsforskning, hereafter SSVL), established in 1969. The motive for creating the two new platforms was the recognized need for effective collaborative efforts in environmental R&D to manage costs and risks related to emerging stricter environmental requirements. SSVL consisted not only of a broad set of representatives from private companies, research institutions, and industry interest groups, but also of consultants, equipment suppliers, and research institutions outside the immediate sector (Bergquist and Söderholm 2011).

The furthering of green knowledge was accomplished in collaboration also with state agencies, particularly within IVL. The Institute was jointly founded in 1966 by the Swedish government and the Swedish pulp and paper industry in collaboration with other industrial sectors. Its primary assignment was to conduct research on the relationship between industrial production and environmental problems and to identify effective solutions. Closely affiliated with the Institute was the Industry Water and Air Protection Agency (Industrins Vatten och Luftvård AB), a service company that was also established in 1966. Together with SSVL, IVL supported knowledge diffusion and technology development of decisive importance to the green reconstruction of the Swedish PPI from the 1960s through the 1970s and 1980s

Table 4.3 Industry-wide collaborative platforms of the Swedish pulp and paper industry for environmental R&D until 1973

Organisation/Institute	Time period
Sulphate Pulp Committee	1908–1909 (?)
Swedish Pulp and Paper Research Institute (STFI)	1945—Changed name to Innventia AB in 2009
Central Laboratory of the Pulp Industry	1936 (ascended into STFI in 1968/69)
Water Pollution Committee	(1937) 1945–1953/54
Water Laboratory of the Forest Industry (SIV)	1953/55–1964 (was first governed by the Water Protection Committee of the Forest Industries, but in a few years turned into the Forest Industries' Water Protection Council respectively the Forest Industries' Water Protection Research Foundation, which in turn later became SSVL)
Swedish Forest Industries' Water and Air Pollution Research Foundation (SSVL)	1963—still active
Institute for Water and Air Protection (IVL)	1966 (today IVL Swedish Environmental Research Institute)
Service company of IVL	1966 (acquired by the Swedish Steam Boiler Association in 1982)
Energy Committee	1973—still active

Sources Söderholm and Bergquist (2012, 2016)

(Bergquist and Söderholm 2011). Table 4.3 provides an overview of the collaborative platforms.

It should be mentioned that the knowledge generated within IVL and SSVL was applied by the Franchise Board of Environmental Protection (FBEP) while enforcing the EPAct through the issuing of individual permits. The network connected to the environmental R&D activities, including both industry and environmental authorities, hosted technical competence and contributed to a shared understanding of reasonable courses of action. There were, however, conflicting opinions on how far industry could and should go in terms of environmental compliance.

4.5 Towards ECF and TCF Bleached Pulp

The replacement of elemental chlorine as a bleaching agent with the alternative ECF and TCF methods is an internationally well-known, environment-related technological shift of the PPI. Technically the ECF-process means a complete replacement of chlorine (Cl_2) with chlorine dioxide gas (ClO_2). By replacing Cl_2 with ClO_2 the levels of absorbable organic halogens (AOX) are greatly reduced. The TCF-process in turn completely eliminates the use of both Cl_2 and ClO_2 and instead typically

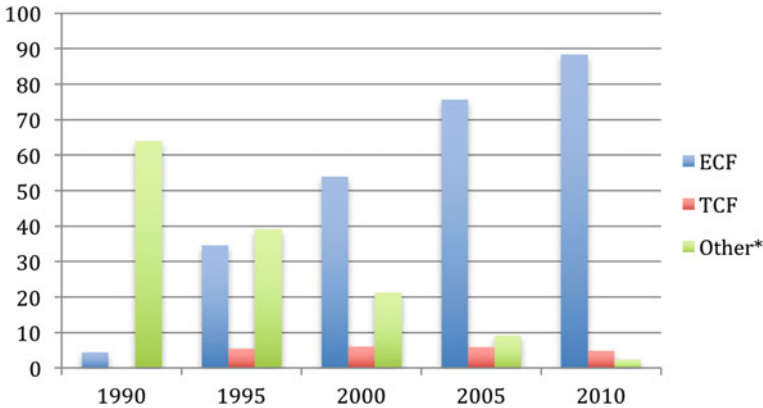


Fig. 4.5 Bleached chemical pulp production in the world 1990–2010 (million tons). *Source* Alliance for Environmental Technology (2012). *Pulp bleached with some molecular chlorine

uses hydrogen peroxide (H_2O_2) and/or ozone (O_3) as substitute bleaching agents. The development of ECF and TCF was further aided by improvements in the oxygen delignification technology, which is used in a pre-bleaching stage.

The shift towards alternative bleaching methods was dramatic. Soon after the US EPA in 1985 detected low concentrations of the extremely toxic and highly chlorinated hydrocarbon group dioxins in fish caught downstream from a few pulp mills, Swedish environmental authorities immediately followed up with their own investigations. In 1986, they concluded that crabs collected near the effluent site of a Swedish pulp mill contained dioxins, too. In the years to come the issue of bleached pulp was raised on both public and governmental agendas throughout the world and regulatory processes were initiated in pulp producing countries. Hence, the risks of dioxin were intensively discussed during the European environmental debate and Sweden was, already in 1988, the first country in the world to set up a regulatory standard for controlling dioxins discharged from pulp mills (Bergquist and Söderholm 2015). Until recently the dioxin alarm has caused a major shift in bleaching technologies worldwide. In 1990, 93% of the bleached pulp produced in the world was bleached by elemental chlorine and in 2010, this figure had dropped to only 2.7%. Figure 4.5 illustrates this development.

It is widely recognized that the technologies diffused more rapidly in the Nordic countries compared to North America, and it is mainly explained by the rise of green consumerism in key markets for Nordic producers while the demand for chlorine free paper was absent in North America (Marcus 1999; Smith and Rajotte 2001; Harrison 2002; Norberg-Bohm and Rossi 1998; Reinstaller 2005; Smith 1997; Popp et al. 2011). Figure 4.6 illustrates the diffusion of ECF and TCF in the Nordic countries since 1990.

Yet, it gives a highly simplified picture to bundle the Nordic countries in this respect. It is rarely highlighted that the great majority of the pulp producers a few

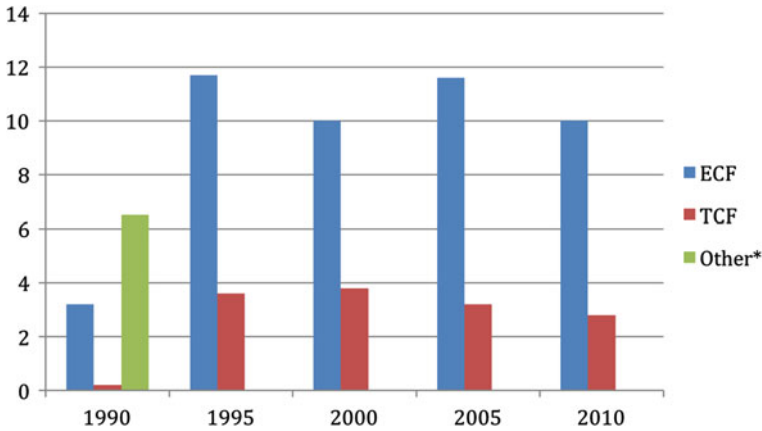


Fig. 4.6 Bleached chemical pulp production in the Nordic countries 1990–2010 (million tons). *Source* Alliance for Environmental Technology (AET) (2012). *Pulp bleached with some molecular chlorine

years into the 1990s that had switched to TCF were of Swedish origin and only two were Finnish (Reinstaller 2005, p. 1373). Moreover, Swedish producers, unlike Finnish ones, pioneered in the development of several core technologies for the ECF and TCF processes in the 1970s and 1980s, such as oxygen delignification, advanced batch cooking and ozone bleaching (Kramer 2000). The pioneering development of the Swedish producers in this matter should be viewed in the collaborative context of the long-term environmental R&D activities discussed above, and where important technological steps were achieved through networks of actors rather than by single firms. Thus, already from the mid-1970s, projects were initiated within both SSVL and the Swedish Pulp and Paper Research Institute (STFI) that focused largely on improving the pulp bleaching process.

The projects typically aimed at decreasing the use of chemicals while increasing the level of delignification in the boiler and in the subsequent oxygen delignification. The main motives in these instances were both to decrease costs and cut emissions from the bleaching process. Thus, already in the early 1970s a pilot plant for oxygen delignification was constructed at a Swedish mill in relation to a SSVL-project (Jerkeman 2007), and two decades later the technology was installed at all Swedish pulp mills (SSVL 1991). At the time, the Nordic Council of Ministers considered the oxygen delignification technology the single most effective process-oriented device to reduce chlorinated organic compounds (Nordic Council of Ministers 1989, pp. 21–23). Also during the 1980s, methods of boiling the pulp to very low levels of lignin, which in turn reduced the need for bleaching chemicals even further (Modified Continuous Cooking/Super Batch Cooking), were developed jointly (and later widely diffused) in the Swedish PPI (Jirvall and Noodapera 1995).

Industrial pollution was regulated only in a limited way in Finland before the late 1980s, and the preferred method for controlling it was by end-of-pipe technology and

particularly the activated sludge method. In 1989, it was applied by a large number of Finnish sulphate/kraft pulp mills, whereas Swedish mills instead were better outfitted with pollution prevention methods such as oxygen delignification, modified cooking and high chlorine dioxide substitution (Auer 1996). Hence, before green consumerism grew in key markets for Nordic producers in the 1990s, regulation was the main trigger for the technological shift towards ECF and TCF among Swedish pulp mills. The Swedish FBEP took an initial and clear standpoint on the dioxin issue already in 1986, when it delivered final conditions for a sulphate pulp mill that declared that the wastewater from the bleaching process caused significant local damage to water-based organisms. In 1988, the Swedish Parliament in turn adopted a proposal which stipulated that industrial emissions of chlorinated organic compounds must be reduced to 1.5 kg AOX/ton of pulp (the normal emission level was about 4 kg per ton of pulp at this time). At this stage the Swedish Forest Industries Federation identified necessary investments to meet the requirements that were now being enforced to be 4 billion SEK, and for some mills it represented up to 50% of the annual investments until 1992 (Bergquist and Söderholm 2015).

The final important technological steps towards TCF pulp were taken by the Swedish PPI in the very last years of the 1980s due to rather forceful regulatory action. In 1988 the Swedish government imposed on an individual mill the most stringent standards ever, namely a maximum of 0.5 kg AOX per ton. The mill, Aspa, was a small producer of market pulp, however, with a sensitive location on a lake that supplied drinking water for several communities. Already in the spring of 1989 the mill had installed a method which produced these low emissions, however, after further development work and only a year later the so called Lignox process⁷ allowed for the production of TCF pulp. Hence, the small Swedish firm ASPA was the first mill in the world to produce TCF pulp. Still, it is important to note that while the development work physically took place at ASPA, the knowledge underpinning the transition stemmed from the long-term, industry-wide R&D collaboration described above (Bergquist and Söderholm 2015). In 1991, ASPA would, in collaboration with Greenpeace, produce an exact copy of “Das Plagiat”, the weekly *Der Spiegel* printed on paper made of such pulp. It was the first time a magazine was published on chlorine-free paper and this accomplishment has been recognized as having had a great impact on the German public and, by extension, also the greater northern European market (Waluszewski and Håkansson 2004). For the first time it was possible to market paper products with eco-labelling, an opportunity which the Swedish producers quickly embraced. At this time the Swedish Nature Conservation Association had launched two environmental classes (“low chlorine” and “chlorine-free”) for bleached paper qualities which got major impact and helped the Swedish pulp producers in their first-time marketing of green products by this new ‘eco-labelling’ standard (i.e., chlorine-free pulp and paper products) (Bergquist and Söderholm 2015).

⁷The Lignox process: oxygen-bleached pulp is treated with hydrogen peroxide at high temperatures after the removal of heavy metals with a complexing agent. Subsequent final bleaching takes place with peroxide and chlorine dioxide.

In 1994 the majority of the Nordic mills that had switched to TCF were of Swedish origin (remaining Swedish mills had all switched to ECF). In contrast, only two mills in Finland had opted for TCF by this time. Also in the US, the companies showed little interest in shifting to TCF. Only two mills had adopted TCF in 1994 (Reinstaller 2005, p. 1373). Thus, also in the US the policy process moved more slowly and when the Swedish PPI aimed to produce ECF and TCF pulp in the early 1990s the US EPA still worked on defining the standard settings for controlling dioxin emissions. For the US PPI, the dioxin issue meant something completely new as the mills could not compel only by installing end-of-pipe treatments, but had to invest significant funds in adopting new bleaching technology. The US industry had never had a strategy to deal with pollution with internal process changes (Gunningham et al. 2003, p. 16; see also Smith 1997). Thus, resistance to making the change was strong within the sector because it would come both at a very high cost and without any advantages on the American market (Reinstaller 2005, 1380). This helps explain why Greenpeace failed in its attempt in 1992 to convince the American *Time* magazine to switch to publishing on TCF paper. Further, Georgia Pacific, one of the leading pulp and paper producers in the US, announced in 1992 to consumers that it would not market TCF pulp, having decided to invest in chlorine dioxide substitution instead. Customers who wanted TCF pulps would have to seek other suppliers. This was possible for the company to do and say as the demand for TCF pulp was very low on the US market (Smith 1997, p. 131). And together with a slower regulatory process, US firms could wait to alter the technology. In this context, in 1989 the US Office of Technology Assessment (OTA) reported on the compliance of Swedish pulp mills to more stringent standards of chlorinated organics, whereas it was unreasonable to hold US firms to such standards due to both economic risks and scientific uncertainties (Powell 1997, p. 12).

In sum, although the shift towards ECF and TCF apparently happened swiftly in the Swedish case, the development-path towards environmentally friendlier bleaching methods was the outcome of decades-long industrial efforts to increase efficiency and reduce the use of chemicals by changing internal processes, in combination with long-term and continuously strengthened environmental legislation.

4.6 Energy Transition

In parallel to the “greening” of industry with respect to increased pollution control, two other issues have had a major impact on the greening of the PPI since the early 1970s. The first is the increased energy prices in the wake of the oil crises of the 1970s and the second is the fear of a shortage of wood. Neither issue was initially related to environmental concerns, but became increasingly so as they drove serious concerns about energy use and triggered energy savings as well as recycling.

Indeed, pulp and paper production is energy-intensive. The PPI is the largest energy user in Sweden and accounts for 52% of the total industrial energy use (SEA 2017, p. 21). In the EU the PPI accounts for 14% of the total industrial energy

use (Jönsson 2011). Although energy usage was always important to the PPI due to its cost, the 1970s caused the need for energy savings and finding substitutes for oil to become preeminent concerns, and both the Swedish PPI and the Swedish government turned their attention to phasing out oil from pulp and paper production. As a consequence, the energy mix of the Swedish PPI underwent radical changes over the 1970s and 1980s, and a large-scale substitution of oil took place. In 1973, for instance, oil accounted for 43% of the total external energy use and in 1984 the share of oil had decreased to 16%. Moreover, in 2011 the corresponding number was 5% (Skogsindustrierna 2012).

Oil reduction was mainly achieved through increased use of internal biofuels (external biofuels remained fairly constant); between 1973 and 1984 the share of energy generated from internal biofuels increased from 55 to 72%, and in 2011 the share of biofuels was 79% (Fig. 4.7). The biofuels mainly consisted of by-products from the pulp manufacturing process, where the biggest share is generated from black liquor⁸ and the rest from bark and wood residues (Federation of Swedish Forest Industry 2012). The overall reduction in the use of oil was also made possible through other energy efficiency improvements and increased internal production of electricity through back-pressure turbine power generation (Lindmark et al. 2011; Bergquist and Söderholm 2016). Of central importance for this development, which included a great deal of incremental technology development, was the already established collaborative strategy of firms within the industry and between the PPI and state authorities. Thus, a large number of energy projects were subsequently conducted through inter-firm and state-industry collaborative R&D platforms established after the 1940s, such as STFI and SSVL (Table 4.3). Still, to manage the new energy challenge the Swedish PPI had already appointed in 1973 a standing Energy committee consisting of 12 members from among management and technical personnel within the sector.

Between 1973 and 1977, no fewer than 51 new energy projects had been initiated or at least proposed within the sector. These involved 37 energy conservation and 14 energy generation projects, most conducted/proposed in collaboration with organisations closely associated with the sector, such as STFI, the Swedish Cellulose and Paper Mill Association (SCPF), and the Steam Generator Association (in Swedish Ångpanneföreningen), but also universities and research institutes outside the sector (e.g., the Thermal Engineering Research Institute (in Swedish Värmeforsk) (Marklund 1994, p. 143). Underpinning the energy transition of the Swedish PPI was also a proactive governmental strategy to emphasize knowledge management and collaboration with industry along with the substitution of oil with internal biofuels. The Swedish government assigned significant subsidies for prototypes and demonstration plants by its energy policy decision in 1975, and such activities increased greatly over time. In the 1970s, new processes and technologies on a factory-wide scale could be subsidised by as much as 50% (Bergquist and Söderholm 2016).

⁸In the pulping process, cooking chemicals, known as white liquor are used to break out and dissolve the lignin whereas the white liquor becomes black liquor. There are basically two main process streams coming out of a pulp mill: cellulose fibres and black liquor.

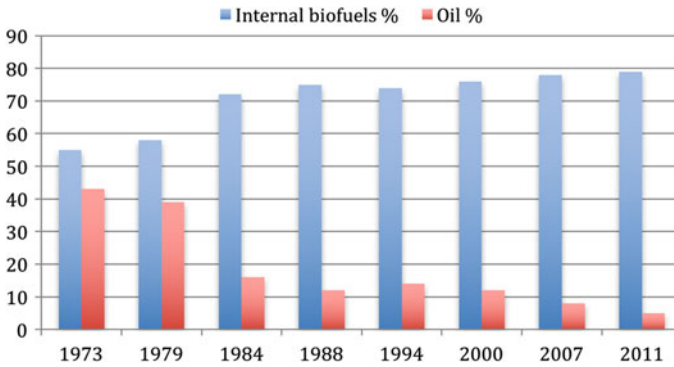


Fig. 4.7 Consumption of internal biofuels and oil in the Swedish pulp and paper industry 1973–2011 (% of total energy use). *Source* Skogsindustrierna (2012)

The energy transition of the Swedish PPI was further driven by the fact that focus was directed towards unutilized potential energy sources, whereby a previous waste problem with bark and chips now could be transformed into energy savings and improved energy efficiency. Moreover, the PPI feared shortages of wood and sought means of increasing its energy efficiency, and these forces led it to increase its use of recycled paper in pulp production; producing pulp from recycled paper requires only one-fifth of the energy needed produce it from virgin wood. Thus, from not have being utilised at all in Swedish pulp production prior to 1975, recycled paper came to be an important raw material. Of central importance for this development were improved methods for removing ink and other contaminants, such as plastic, from the recycled paper, and the introduction in 1975 of a compulsory collection system for old newsprint from households (Bergquist and Söderholm 2016).

The improved energy efficiency over the 1970s and 1980s coincided with an on-going structural change in industry, namely a trend towards fewer and larger production units and an improved ability to take advantage of economies of scale (Järvinen et al. 2012). The concentration of production units allowed, among other things, a higher degree of integrated pulp and paper production whereby the energy intensive step of drying the pulp (at the pulp mill, only to dissolve it again at the paper mill) was avoided (Bergquist and Söderholm 2016).

Today the energy efficiency of the Swedish (and Finnish) PPI is higher than that of other major pulp producing countries such as Brazil, the US and Canada (Fracoro et al. 2012). However, the sector's total energy use has stayed relatively constant due to considerable production expansion, not the least in mechanical pulp, which has contributed to increased use of electricity beginning in the early 1980s (Bergquist and Söderholm 2016). As a result, between 1973 and 2011 the total energy consumption of the Swedish PPI increased from 55 to 57 TWh (Skogsindustrierna 2012).

4.7 Environmentally Driven Transformation—The Past and the Future

Over the second half of the twentieth century, environmentally related issues have played a central role in the overall transformation of the Swedish PPI, essentially as new or altered technologies were required to comply with tightening environmental regulations. In the Swedish context, the greening of polluting manufacturing industries occurred within a collaborative regulatory framework. Knowledge was flowing quite openly between Swedish PPI companies and between environmental authorities and the regulated industry (Bergquist and Söderholm 2011). Thus, the significant environmental improvements accomplished within the Swedish PPI over the period can only be fully comprehended by acknowledging the role of collaborative environmental R&D activities among firms within the sector and between the sector and the state. Furthermore, the development after the 1980s illustrates how the emergence of green consumerism came to play a role as a driver towards environmental improvements.

The PPI has developed from being considered one of the greatest polluters of the twentieth century to an industry that is essential for the transition towards a more sustainable (bio-based) economy. In the EU, the PPI today already constitutes the biggest single industrial producer and user of renewable energy; 56% of the industry's primary annual energy consumption is bio-based (CEPI 2013, p. 50). And there are big hopes, especially within the Nordic countries, that the PPI will take the lead in clean-tech innovation and green growth in terms of new products and the second generation of "green" fuels. The trend is global and most pulp and paper companies are working in this direction. The sector, particularly in Sweden, is at the same time undergoing substantial change due to stricter environmental regulations, unstable oil price, energy policies, global competitiveness and structural changes. In addition, the increasing use of electronic rather than paper-based communications are pushing the PPI towards self-renewal to improve its profitability (Backlund and Nordström 2014), whereby it appears as if parts of the pulp industry have experienced a shift towards becoming more "biorefineries" than pulp producers (Hamaguchi et al. 2012). One promising technology in this context is black liquor gasification (BLG⁹) for the production of fossil free transportation fuels. Here the Swedish company Chemrec has been a key player. Thus, in 2009 and after 20 years of R&D on BLG, Chemrec constructed a pilot plant with financial support from the European Community's Framework Programmes and the Swedish Energy Agency. However, after the BLG demonstration technology did not develop as expected and there was a lack of investment interest in the project, the pilot plant was shut down and remains so. One suggested reason for the lack of interest was the uncertain market conditions for biodiesel and methanol (SEA 2016). Still estimates suggest that BLG could supply as much as 7% of Sweden's total—not merely its industrial—demand for electricity, or as much as 30% of the nation's demand for transportation fuels. Outside the

⁹BLG is in its essence a process in which a clean synthesis gas is produced from black liquor by converting its biomass content into gaseous energy carriers (Bajpai 2014, p. 3).

Nordic countries, BLG technology is also developing in the US and Asian pulp producing countries (Bajpai 2014, pp. 4–5). Another example of on-gong renewals is the Finnish Metsä Group's investment in the 'bioproduct' mill in Äänekoski, Central Finland, which represents the largest forestry investment ever made in Europe, with a value of EUR 1.2 billion. It is the first next-generation product mill in the world, where the production of energy, along with the pulp production, play a crucial role (Metsä Group 2017).

Another trend in the PPI's development towards environmental improvements, partly from new products within the area of bioenergy, is a continued expansion of the traditional pulp and paper production driven by an increased global demand for cardboard and sanitary papers. For example, the Swedish pulp and paper company SCA is currently rebuilding its Östrand mill (due to start up in 2018) in Sweden and has publicized that a large-scale investment programme will lead to 'the largest production line for bleached softwood sulphate pulp in the world'. Above all the firm has stressed that the mill will become 'world class in terms of product quality, environment and competitiveness' by becoming 'the leader in terms of resource management' and 'generate surplus energy' to be sold in the form of 'green electricity and district heating'. Also, 'both TCF and ECF pulp' will be produced with raw materials from 'sustainable forestry'.¹⁰ Overall the Swedish example illustrates, however, that the transition towards cleaner and more energy efficient pulp and paper production is the result of long-term and incremental processes, whereby the technology development has been shaped by both evolving markets, long-term collaborative R&D and shifting concerns in society about the natural environment and human well-being.

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¹⁰<https://www.sca.com/sv/massa/aktuellt-inom-pulp/expansion-av-ostrand/>. Accessed 19 January 2018.

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THE ROLE OF CHLORINE IN DIOXIN FORMATION

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There is poor correlation between total chlorine in waste streams and formation of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) during waste combustion. This is because the active chlorine (Cl) species are strongly dependent upon combustion conditions. For homogeneous conditions, trace amounts of a hydrocarbon species (benzene) injected into the effluent from complete combustion of a mixed chlorocarbon fuel (ethylene and chloromethane) results in formation of stable, oxygenated and chlorinated compounds. This occurs over a broad range of temperatures (400–900°C), provided that a fraction of the system chlorine is in the Cl radical form. Cl is the only form in which chlorine can react, in gas-phase, with stable hydrocarbon species, and these reactions are very fast, even in the low temperature regime. Molecular chlorine (Cl₂) may subsequently participate in reactions with carbon-based radicals, and these reactions are the primary source of chlorinated products. Hydrogen chloride (HCl)—the major chlorine species in the products—can react with oxidizing radicals (eg, OH) and promptly form significant amounts of Cl. Gas temperature has a great influence on the final distribution of products. At 800–900°C, practically all of the benzene which was attacked by Cl is converted to carbon monoxide and small unsaturated hydrocarbons by subsequent reactions with oxygen. At about 750°C, measurable concentrations of chlorobenzenes are formed. At lower temperatures (400–600°C), chlorophenols become a large fraction (up to 15%) of the total reacted benzene. Heterogeneous reactions result in the formation of Cl₂ through catalyzed reactions (most actively by copper salts) and promotion of carbon-Cl bond formation. The latter is dependent on the ash surface species and type, ash adsorptive characteristics, temperature, and presence of regenerative Cl in the waste combustion products.

Keywords: polychlorinated dibenzodioxin; dibenzofuran; air pollution; combustion; chlorination.

INTRODUCTION

The public concern with the emissions of 'dioxins' or polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) from incinerators has resulted in periodic calls for the banning of chlorine from waste streams. This paper reviews the mechanisms for the formation of dioxins to try to establish a better understanding of the role of chlorine in the dioxin formation process in order to guide both control measures and regulations on the composition of the waste stream.

The formation of PCDD/F as trace by-product pollutants from combustion processes has been extensively studied over the last 15 years. These chemicals are highly persistent, bioaccumulating in the environment and ending up in the food chain. The more toxic form has been classified as a 'known' human carcinogen¹, and they have been linked with tumour formation, learning deficits, endometriosis, immunosuppression, and developmental/reproductive effects^{2,3} in experimental animals.

PCDD and PCDF are each composed of eight homologue groups (mono through octa), distinguished by the number of chlorine (Cl) atoms attached to their ring structures. The eight homologue groups have varying numbers of structural isomers, totalling 210 congeners (75 of PCDD, 135 of PCDF). Of these 210, 17 are considered toxic to varying degrees due to their biological activity, and each is

Cl-substituted in at least the 2,3,7,8 positions. Each of these 2,3,7,8 isomers has been assigned a toxicity equivalency factor (TEF) which, when combined with the concentration, produces a weighted toxic equivalency (TEQ) of the mixture.

The occurrence of PCDD/F in the environment, as deduced from the depth profiling in sediments, has grown dramatically since the 1930s in parallel with the growth with the production of chlorinated organic compounds⁴. This has led to the attribution of the dioxins to primarily anthropogenic sources with incineration implicated as a major source⁵. The dioxins are widely distributed globally⁶ with the concentrations being generally highest in industrialized countries.

Despite the predominance of PCDD/F from combustion sources, our understanding of the formation mechanisms and reaction rates in combustion systems has not yet reached the point where we can predict the potential of a system to form PCDD/F or take adequate measures to substantively prevent formation. This is due to the extremely difficult nature of the reaction mechanism: only trace concentrations of products are formed; multiple gas- and solid-phase reactions are involved; the combustor reaction environment is difficult to simulate; the reactants themselves are present at only trace concentrations; simultaneous chlorination, dechlorination, formation, and decomposition reactions occur; and monitoring PCDD/F

formation is possible only through application of long and difficult manual sampling methods and costly chemical analyses.

THEORIES AND FACTORS

PCDD/F are formed via both homogeneous and heterogeneous processes with the heterogeneous pathway generally considered to be the more important. There are two main mechanistic theories to account for observed PCDD/F heterogeneous formation of which the distinction is likely to be blurred by further research. The first theory is the so-called 'de novo synthesis' mechanism which has been postulated and demonstrated by Stieglitz and coworkers⁷. In this mechanism, the presence of fly ash containing unburnt aromatic moieties and metal catalysts is essential. Gas-phase Cl, likely as hydrogen chloride (HCl), is said to form metal-chloride ligands on the fly ash surface, after which Cl is transferred to carbon (C). The subsequent metal-catalysed oxidation/gasification of the fly ash surface releases these C-Cl structures, some of which comprise the subject PCDD/F pollutants, and others which form related compounds such as chlorophenols, chlorobenzenes, and non-aromatic chlorinated hydrocarbons. The second theory is the so-called 'precursor' theory which has been demonstrated by Dickson and Karasek⁸ and Karasek and Dickson⁹. In this mechanism, combustion byproducts including compounds such as chlorophenol or chlorobenzenes react on the catalyst-laden fly ash surfaces to form PCDD/F through condensation reactions. More recently, it has been demonstrated¹⁰ that polycyclic aromatic hydrocarbons (PAHs) also chlorinate and decouple to form isomer-specific PCDD/F compounds. Both of these theories have been adequately validated in laboratory experiments. Arguments based on relative reaction rates, product congener profile comparisons, and temperature dependencies have been used to support both theories. The relevance of each of the theories, however, is difficult to ascertain: laboratory simulations of assumed microscale phenomena leave considerable doubt regarding their ability to replicate or represent conditions in a practical combustion system. The actual situation may be such that the carbon source is derived from both condensing, gas-phase organics and volatilizing, fly-ash-derived organics, the relative magnitude of which is due to system- and operational-specific variables but both of which subsequently participate in the same, or a similar, reaction mechanism.

At any rate, the generally requisite conditions for formation of PCDD/F are: (1) incomplete combustion of an organic fuel; (2) the presence of trace metals and surfaces to act as catalysts; (3) a temperature/time history providing at least 1 s below 600°C; and (4) a source of Cl. The focus in this paper will be Cl: evolution of various Cl species, Cl species concentrations and temperature/time dependency, mechanisms in carbon chlorination, and combustion factors that affect Cl species.

CORRELATION OF PCDD/F WITH CHLORINE IN WASTE

Data from some 169 municipal waste combustors, hazardous waste incinerators, medical waste incinerators, cement kilns, hazardous-waste-fired boilers, biomass combustors,

and laboratory- and pilot-scale combustors were examined to determine if there was a correlation between the chlorine content in the feed and the PCDD/F concentrations in the stack¹¹. The chlorine content in the feed varied from less than 0.1% for some biomass combustors to over 80% for some hazardous waste incinerators. The chlorine in the waste stream was in the form of inorganic salts as well as synthetic organic products including polyvinyl chloride (PVC). The results of the statistical analysis of the data showed that there was no significant effect of chlorine in the feed and the PCDD/F concentrations in the stack for field data although well controlled laboratory experiments showed an increasing concentration of PCDD/F with inlet chlorine content. The conclusion of the study was that in field studies the effects of confounding variables such as the temperature of the particulate control device, the excess air, and other combustor operating conditions masked any effect of the chlorine content in the feed. In order to understand such data, it is therefore important to understand what the active form of chlorine is and how it is influenced by changes in design and operating conditions of combustors and air pollution control devices.

Chlorine is undeniably required for formation of PCDD/F but only trace amounts in the fuel feed are needed to provide the minimum amount. For example, while emissions of PCDD/F from coal combustion are generally considered to be low, if measurable, even coal with less than 1 ppt (part per trillion, 1×10^{-12}) of Cl has more than sufficient Cl to produce PCDD/F that would exceed common regulatory limits. So the relevant question is not what amount of chlorine is limiting but what are the pathways for PCDD/F versus other chlorinated pollutants?

Homogeneous Formation

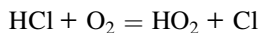
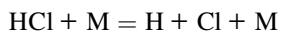
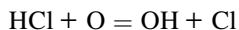
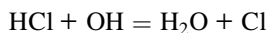
Which form of chlorine favours the formation of chlorinated hydrocarbons and PCDD/F?

The three forms of chlorine present in the post-combustion products of organic wastes are HCl, Cl, and chlorine (Cl₂). The hypothesis, for which support will be provided, is that the active form of chlorine is atomic chlorine and not total chlorine and that the concentrations of chlorinated hydrocarbons can be changed significantly by manipulating post-combustion conditions to modify the concentrations of either the atomic chlorine or hydrocarbon intermediates.

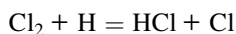
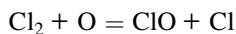
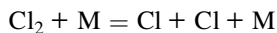
While the majority of the system chlorine in the products is in the HCl form, a non-negligible fraction may be present as Cl radicals and Cl₂. These two species (as opposed to HCl, which has very little reactivity in the combustion environment) can react with organic compounds. Cl radicals can readily abstract H atoms from stable hydrocarbons, forming carbon-based radicals and HCl. At high temperatures, 1400–1500°C, equilibrium indicates that a minor, but not negligible, fraction of the total system chlorine is in the Cl radical form. Furthermore, kinetic constraints may cause the persistence of high concentrations of Cl radicals, which exit the primary zone of chlorocarbon flames. The high concentrations of Cl radicals that survive during the cool-down of combustion products can promote the fast, gas-phase formation of chlorinated and oxychlorinated pollutants, under conditions possibly arising during practical combustion processes.

The concentrations of HCl, Cl, and Cl₂ can be calculated for different conditions by taking the following reactions into account.

Interconversion reactions of Cl and HCl:



Interconversion reactions of Cl and Cl₂:



The kinetics of the reactions are relatively well understood, and the concentration of Cl and Cl₂ can be calculated with fair confidence^{12,13}. The factors that favour high chlorine concentrations are: (1) high temperatures; (2) rapid cooling from high temperatures because of the slow rate of recombination of the chlorine atoms; and (3) high oxygen or OH concentrations because of their abstraction of H from HCl.

As the temperatures are reduced, the atomic chlorine recombines to form Cl₂. High concentrations of molecular chlorine in combustion products are therefore an indirect measure of high concentrations of atomic chlorine.

What conditions favour the formation of chlorinated hydrocarbons?

The reaction of chlorine atoms with hydrocarbons in the presence of oxygen will depend upon the temperature of reaction. This will be demonstrated here by summarizing results by the authors of injecting benzene into the lean post-flame combustion products of a chlorinated hydrocarbon after the combustion products had been cooled to different temperatures¹³.

High-temperature oxidation: At 1100°C, benzene was promptly oxidized and converted to CO₂ (Figure 1-a). At the same time, a significant increase in the concentration of Cl₂ in the quenched samples was observed (Figure 1-b) indicating that new Cl radicals were generated by the reaction of HCl with oxygen-containing radicals (primarily OH). The OH radicals needed to drive this process were those generated during the full oxidation of the carbon species. These results indicate that benzene was oxidized primarily by the initial attack of oxygen species. H abstraction by Cl radicals certainly occurred, at least to some extent, and the resulting phenyl radicals were completely oxidized to carbon dioxide (CO₂). It can be concluded that, due to the high temperature, only the products of the complete oxidation of benzene were formed.

Intermediate temperature reactions: A similar experiment conducted at 900°C (Figure 1-a) showed that about 100 ppm of benzene is initially consumed and converted to smaller secondary products (primarily carbon monoxide (CO), acetylene, and vinyl acetylene). After the initial phase (0–2 ms), benzene oxidation continues at a much slower

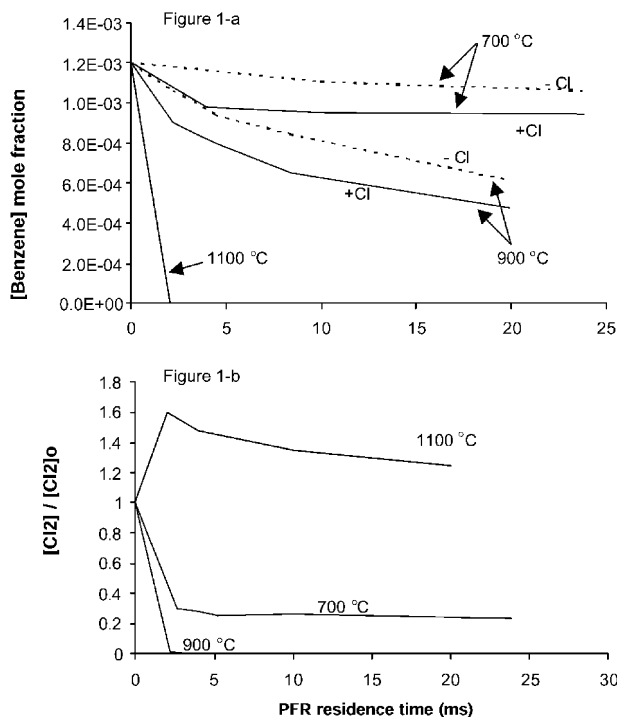
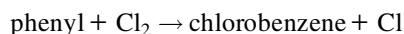


Figure 1. Concentration profiles of benzene (Figure 1-a), and Cl₂ (Figure 1-b) in quenched combustion products. Measurements relative to three different plug flow reactor (PFR) temperatures (700, 900, and 1100°C) are reported. For benzene measurements, data relative to control experiments (dashed lines labelled '-Cl') are also reported. During the control experiments, no chloromethane (ie, the only chlorine source) was fed to the primary reactor stage and the benzene concentration was measured. The comparison of the benzene profiles with and without chlorine in the system allows one to estimate the fraction of benzene which was consumed through the direct interaction with chlorine species. In Figure 1-b, data on Cl₂ concentration refer to the measurements in quenched combustion gas and are normalized with the Cl₂ concentrations measured just upstream of the secondary benzene injection. The initial values of the Cl₂ mole fractions are 1.6×10^{-4} , 1.4×10^{-4} , and 1.1×10^{-4} , respectively, for the 1100, 900, and 700°C measurements.

rate, yielding an increasing amount of the same secondary products. Given the relatively low temperature, the oxidation process was not complete and, after a residence time of 25 ms, no measurable CO₂ production was observed. A parallel decrease in the concentration of Cl₂ in the quenched products (Figure 1-b) indicates that the initial benzene consumption occurred through reactions with Cl radicals. The likely products of the reaction of benzene and Cl were HCl and phenyl radicals. The latter were subsequently attacked by oxygen species and converted to secondary products. Chlorobenzene, the only chlorinated product of incomplete combustion (PIC) observed, accounted for just a minor, although non-negligible, fraction of the conversion products (about 1.5 ppm mole fraction, which was equivalent to 1.5% of the total benzene consumed). Chlorobenzene may have formed, at least in part, by the reaction:



Lower reaction temperatures: A third experiment was conducted at 700°C and, this time, benzene consumption was observed practically only in the initial phase of the process (Figure 1-a). The product distribution included the same secondary reaction products observed at 900°C

and a much larger fraction of chlorinated or oxychlorinated species (the sum of the concentrations of chlorobenzene, 2-chlorophenol, and 4-chlorophenol, measured after a residence time of 25 ms, accounted for about 12% of the total benzene consumed). The concentration profile of Cl₂ (measured in the quenched samples) showed a different pattern than in the two previous cases. After a prompt decrease in mole fraction to about one fourth of the initial concentration, the Cl₂ level remained practically constant. This indicates that, in fact, not all the Cl₂ measured in the quenched products sampled before the benzene injection was, at 700°C, in the form of Cl, but only about three-fourths.

The above results are consistent with the following mechanism:

- (1) At a low enough temperature (eg, 700°C), benzene reacts with chlorine species and oxygen in a process initiated either by H abstraction by Cl radicals or via Cl attack on the benzene ring.
- (2) The resulting radical further reacts with oxygen, yielding secondary products and chlorophenols, or can react with Cl₂, yielding chlorobenzene. Chlorobenzene might also be formed by the recombination of phenyl and Cl radicals.

Can chlorinated hydrocarbon formation be controlled by controlling the chlorine atom concentration?

Support for the above role of chlorine atoms has been obtained by injecting ethylene upstream of the benzene addition. If ethylene is injected at 1250°C, it burns and generates OH which augments the Cl atom concentration through the reaction OH + HCl = Cl + H₂O. In this case the production of chlorobenzene and chlorophenols was augmented by a factor equal to the increase in Cl atom concentration. If the ethylene is injected in the lower temperature regime, again upstream of the benzene injection, it will react with and consume the chlorine radicals. In this case, the chlorobenzene and chlorophenol consumption is suppressed.

What determines polychlorination?

Chlorine atoms in the lower temperature regime are the source of chlorination. As long as the concentration of the hydrocarbon injected is greater than that of the chlorine atom, monochlorinated hydrocarbons will result. Polychlorinated products are produced once the chlorine atom concentration exceeds that of the hydrocarbon.

Heterogeneous Formation

The mechanism of carbon chlorination is a significant question relating to an understanding of the mechanism of chlorinated organic formation.

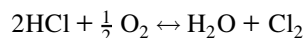
Is a fuel or waste C-Cl bond required for subsequent formation?

With an understanding that PCDD/F emissions are due to formation processes in the combustor and not simply the result of incomplete combustion of a PCDD/F-containing feed stock, the next likely question concerns whether organic Cl is necessary for formation. This is a contentious issue, particularly regarding the role of specific forms of chlorinated organics, mainly PVC.

Numerous studies (eg, Wikström *et al.*¹⁴) have shown that inorganic chloride sources are comparatively equivalent to organic chloride sources for formation of PCDD/F. This suggests that pre-existing C-Cl bonds are not necessary for formation; chlorination readily occurs in the combustion process. This apparent equivalency may be partly understood by studying the role of inorganic chlorides in producing HCl in combustors. Experiments by Uchida *et al.*¹⁵ showed that high temperature (>700°C) production of HCl from alkaline and alkaline earth chlorides occurs and is promoted by the presence of alumina (Al₂O₃) and silicon dioxide (SiO₂), common compounds in fly ash. If the presence of HCl then (at least) partially determines the extent of formation of PCDD/F, then even inorganic chlorides can lead to PCDD/F emissions.

Can gas-phase chlorination occur at lower temperatures?

Direct, quantitative chlorination of phenol by gas-phase Cl₂ has been demonstrated^{16,17,18} with a maximum at 400°C; significantly less chlorination was observed using HCl as the Cl source (at a maximum of 600°C). As temperatures cool, equilibrium predicts the dominant Cl species to be Cl₂. However, the rate of Cl₂ formation is extremely slow such that most Cl is in the form of HCl as it leaves the stack. It has been hypothesized¹⁹ that some Cl₂ forms as the result of a surface-catalysed reaction (the 'Deacon' reaction) between HCl and O₂:



This first-order reaction occurs¹⁶ with high yields, and the Cu catalyst can be reactivated by addition of HCl to the system. More rapid cooling minimizes this reaction²⁰ by slowing the recombination of Cl to Cl₂. This reaction is catalysed by metals, such as CuCl, of various oxidation states. Gullett *et al.*¹⁷ analysed Cu₂O, CuO, and Cu and found nearly equivalent Deacon activity at a peak temperature equivalent to that of maximum reactivity of Cl₂ with phenol (400°C). No Deacon activity (Cl₂ production) was noted for Fe, Fe₂O₃, and FeCl₂·4H₂O. Fly ash testing indicated that 1.3% of HCl was converted to Cl₂.

Are surfaces necessary for C-Cl bond formation?

Does chlorination occur as a result of gas-solid or solid-solid reactions?

Taylor *et al.*²¹ propose that indirect chlorination of carbon via a transfer from surface Cu occurs as opposed to direct chlorination by gaseous precursors of Cl· or Cl₂. This work, and that of Froese and Hutzinger²², showed that chlorination of acetylene (C₂H₂), a known precursor of aromatics and soot, occurs in the presence of surfaces and a chlorine source. Taylor *et al.*²¹ proposed a surface transfer of Cl from CuCl₂ to C₂H₂ to form a chlorovinyl intermediate, with the presence of these surfaces reducing the formation temperature from 700 to 150°C. Formation of this intermediate is the rate limiting step (30.5 kcal mole⁻¹), and it is more energetically favourable than the Deacon process (48.7 kcal mole⁻¹). The authors report this reaction at as low as 150°C with CuCl₂ (although they show significant yields only at temperatures ≈ 300°C), whereas the Deacon process with CuO occurs at temperatures in excess of 300°C. Subsequent Cl transfers result in dichloroethylene or chloroacetylene (Taylor *et al.*²¹). Repetition

of these steps results in production of multiple chlorinated ethylenes or acetylenes. A lack of unchlorinated molecular growth products indicates that chlorination occurred prior to C growth reactions. Regeneration of the CuCl_2 is possible with HCl supply; hence, the metal serves as a stoichiometric oxidant and not a catalyst. The role of CuCl species in PCDD/F formation via Cl transfer is evidenced by variation in the colour of the Cu, reflecting changes in the Cu oxidation states with temperature. This is a plausible pathway, although it does not explain evidence for direct gas-phase chlorination of phenolic precursors (via electrophilic aromatic substitution reactions) nor did the tests account for possible decomposition of the copper chloride into Cl and/or Cl_2 gas (as shown in Gullett *et al.*^{16,17}).

Considerable work (see Chaltrykian²³), mostly in the field of aqueous catalyst reactions, supports the catalytic role of Cu-Cl species in formation of aromatic aldehydes; aryl halides; hydrolysis of chlorobenzene to form phenol and allyl chlorides to form alcohols; transformation of allenes to form halogenated dienes; dimerization, polymerization, and hydrochlorination of acetylene; and dechlorination reactions. Cu readily forms complexes with electron-donating ligands. When multiple ligands are present, equilibrium is determined by the polarizability of the competing ligands. Thus, copper-catalysed reactions are made up of complicated successive reactions consisting of acts of complex formation and break-down into the original components, activation of ligand molecules in the complex, and conversion of ligand molecule in molecules of the final product. This supports the proposed role of copper catalysts as 'transfer' agents for Cl (as indicated by Taylor *et al.*²¹).

Solution chemistry has shown that acetylene in concentrated aqueous solutions of cuprous chloride is extremely reactive. Acetylene polymerization is also possible using an acidified solution of cuprous chloride and ammonium chloride with acetylene²⁴. A number of non-chlorinated products result, including butenyne (C_4H_4) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{H}$ and traces of acetylene hexamer ($\text{C}_{12}\text{H}_{12}$) and chloroderivates. Nieuwland²⁴ hypothesized that one or two acetylene molecules displace the ammonium chloride and enter into the cuprous complex. This complex decomposes to form, possibly, $\text{CH}_2=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}$ which reacts with an unreacted acetylene to form butenyne.

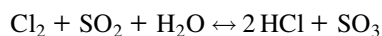
Gas-phase work has also shown the role of copper catalysts. Freidlin *et al.*²⁵ showed the gas-phase hydrolysis reaction of chlorobenzene over silica gel to be greatly enhanced in the presence of CuCl_2 , CuCl, and Cu powder, resulting in the formation of phenol and HCl. Others^{26,27} have measured continuous hydrochlorination of acetylene over dry metal chlorides (Pt, Hg, Cu, Fe, and Ba) supported on activated carbon (180–195°C). Processes to improve vinyl chloride preparation from acetylene and HCl also make use of cuprous chloride.

Similarly, hydrochlorination of butenyne is aided by KCl and NH_4Cl , but mostly by CaCl_2 to form products such as 4-chloro-1,2-butadiene²⁸ and chloropropene²⁹. In the presence of copper salts, a second HCl will be added²⁸. Likewise, dechlorination reactions also occur. The Cu-catalysed dechlorination of tetrachlorophenol was observed when passing H_2 and tetrachlorophenol over cuprous chloride³⁰.

Does PCDD/F suppression by SO_2 act through an effect on the Cl reaction?

The studied effect of sulphur dioxide (SO_2) on preventing formation of PCDD/F may also offer some indirect clues regarding the mechanism and role of Cl in the formation of chlorinated organics. Much research has shown, in bench^{31,32}, pilot^{33,34} and field tests³⁵, that the presence of S, likely as SO_2 , effects suppression of formation of chlorinated organics. This effect may explain why coal-fired boilers, despite sufficient levels of Cl, Cu, organics and particle surfaces, are not significant PCDD/F emitters³⁶.

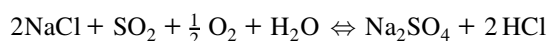
There are several possible hypotheses for mechanistic interference by the S species. It has been proposed¹⁹ and demonstrated at 400°C³² that an effect of S is to deplete the Cl_2 levels through the gas-phase reaction



perhaps through a sulphuryl chloride (SO_2Cl_2) intermediate. This reaction occurs and may be carbon-catalysed. This reaction would presumably inhibit reaction of Cl_2 into aromatic structures via electrophilic aromatic substitution reactions due to reductions in the amount of available Cl. A preliminary concentration effect has been observed such that S/Cl (not Cl_2) ratios around or above, approximately, unity are necessary to produce decreases in PCDD/F formation³⁴.

Another hypothesis suggests that the presence of higher concentrations of sulphur during coal combustion shifts the phase distribution of metallic deposits away from the chlorides necessary for PCDD/F formation. Experimental and equilibrium analyses by Chen *et al.*³⁷ found that the presence of sulphide (added as sodium sulphide, Na_2S) inhibited the formation of the more volatile metallic chlorides, instead resulting in more metallic oxides than chlorides. This may limit the activity of the metal catalysts for PCDD/F formation through reductions in the available metal chloride concentrations. Likewise, equilibrium calculations by Verhulst *et al.*³⁸ similarly show that the presence of S stabilizes many metals in sulphate phases below 800°C. These metal sulphates can displace chlorides; for Cu, the formation of copper sulphate (CuSO_4) completely dominates the formation of copper chloride (CuCl) at temperatures below 500°C. In the absence of S, gaseous Cu_xCl_x species still exist between 300 and 500°C. Increasing Cl levels result in increased Cu volatilization.

Miller and Krause³⁹ also found that chloride salts on wall deposits react with SO_2 and oxygen near the boiler tubes to evolve high concentrations of HCl directly adjacent to the metal. These observations are consistent with work by Uchida *et al.*¹⁵ who found that the presence of SO_2 resulted in the overall reaction ('Hargreave reaction'):



producing HCl(g). The equilibrium constants for these types of reactions increase with decreasing temperatures. An analogous reaction with CuCl or CuCl_2 may be responsible, at least partly, for the reduced formation of PCDD/F observed in combustion systems.

CONCLUSIONS

Major progress has been made in our understanding of the homogeneous and heterogeneous pathways to the polychlorinated hydrocarbons, including PCDD/F. This understanding shows that total chlorine is an imperfect measure of PCDD/F formation potential. For the homogeneous pathway, the concentration of chlorine atoms is the major factor, and its concentration can be augmented by reactions contributing to OH formation or suppressed by hydrocarbon injection of reactants such as hydrogen. The heterogeneous reactions depend on ash surface species and type, ash adsorptive characteristics, temperature, and the presence of regenerative Cl. Knowledge of the chemistry not only explains the imperfect correlation of total chlorine content and PCDD/F formation but can also lead to the development of control strategies which are targeted at suppressing the active chlorine species, either atomic chlorine for the homogeneous pathway or active surface ligands for the heterogeneous pathway.

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ADDRESS

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The South Karelia Air Pollution Study: Acute Health Effects of Malodorous Sulfur Air Pollutants Released by a Pulp Mill

ABSTRACT

We evaluated the acute health effects of a strong emission of malodorous sulfur compounds released from a pulp mill in South Karelia, Finland. The 24-hour ambient air concentrations of hydrogen sulfide for the two emission days were 35 and 43 $\mu\text{g}/\text{m}^3$ (maximum 4-hour 135 and 43 $\mu\text{g}/\text{m}^3$). A questionnaire was distributed after the high exposure and later after a low exposure period to 29 households with 75 subjects living in the nearby community. During the high exposure, 63% of the respondents reported experience of at least one symptom compared to 26% during the reference period. Every third participant reported difficulties in breathing. In the 45 subjects responding to both questionnaires more eye, respiratory and neuropsychological symptoms occurred during the exposure compared to the reference period. The strong malodorous emission from a pulp mill caused an alarming amount of adverse effects in the exposed population. (*Am J Public Health*. 1992;82:603-605)

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Introduction

Large populations in northern Europe and North America are often or constantly exposed to malodorous sulfur air pollutants such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), and methyl sulfides produced by the paper and pulp industry. The knowledge of the adverse effects of these pollutants is sparse, although people living in the neighborhood affected commonly complain of discomfort and express concern about the health effects.

A cluster of paper mills producing wood pulp is located in South Karelia, in southeastern Finland. The two sulfate pulp mills, located in the small city of Imatra (33 000 inhabitants), were, in 1989, estimated to emit annually 2800 tons of H_2S into the air. The annual mean ($2 \mu\text{g}/\text{m}^3$) concentration of sulfur dioxide (SO_2) is low because of the use of natural gas as the source of industrial energy.

During 2 days in September 1987, a strong emission, with H_2S as the major component and mesityloxyde as a minor component, was released from one of the two pulp mills, exposing the local population to intensive catty odor for the 2 days. We evaluated the acute health effects of the emission by comparing the occurrence of symptoms during the high-exposure period and 4 months later during a low-exposure period.

Material and Methods

During the introduction of a new processing technique, a strong malodorous emission was released from the pulp mill using the sulfate method for production, and increased concentrations of H_2S were measured for 2 days at our monitoring station located in a nearby community about 1 km southeast of the source of exposure. The H_2S exposure was measured by absorbing the air sample to cadmium hydroxide.¹ The 4-hour concentrations of H_2S during the high exposure were, on the

average, 4 to 5 times higher, and a maximum of 20 times higher, than the levels before and after the peak emission, during which there was inversion of the air and no wind (Figure 1). The highest 4-hour concentration of H_2S , 135 $\mu\text{g}/\text{m}^3$, was measured at 2 AM. The 24-hour averages for the 2 days were 35 and 43 $\mu\text{g}/\text{m}^3$.

During the peak emission of malodorous sulfur compounds, the mean 1-hour concentration of SO_2 was only 3 $\mu\text{g}/\text{m}^3$. It was not possible to measure mesityloxyde in the ambient air. Mesityloxyde is produced inside pulp mills under the same kinds of conditions that occurred during the peak emission. The presence of mesityloxyde was recognized in the air by its characteristic catty odor.

A reference period of 2 days was chosen about 4 months later, in January 1988. During the 2 reference days no odor was sensed, and the concentration of H_2S was low (0.1 to 3.5 $\mu\text{g}/\text{m}^3$ for 4 hours). The SO_2 concentration was low, 3 $\mu\text{g}/\text{m}^3$, as during the high-exposure period.

An open-ended questionnaire was distributed 10 days after the high exposure to all 29 households of the nearby community; 66 (88%) of a possible 75 subjects responded. Six subjects were excluded because of missing information, leaving 60 subjects: 44 adults (15 men and 29 women; mean age = 45 years and range = 17 to

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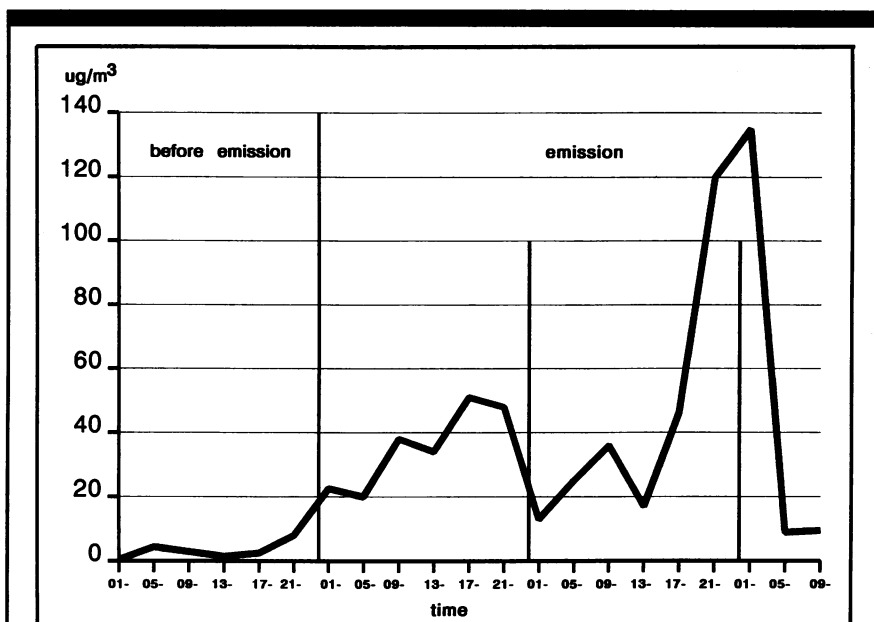


FIGURE 1—Four-hour concentrations of hydrogen sulfide before and during the emission from the first day at 1 AM to the fourth day at 9 AM at the monitoring station located about 1 km from the pulp mill.

TABLE 1—Prevalence of Symptoms in Subjects Who Responded after the High-Exposure Period (n = 60) and after the Reference Period (n = 66)

	High-Exposure Period		Reference Period	
	n	%	n	%
Eye symptoms	13	22	1	2***
Males	5	21	0	0
Females	8	22	1	3
Nasal symptoms	5	8	13	20
Males	2	8	5	16
Females	3	8	8	24
Cough or pharyngeal irritation	9	15	3	5
Males	5	21	1	3
Females	4	11	2	6
Breathlessness	21	35	1	2***
Males	7	29	0	0
Females	14	39	1	3
Nausea	14	23	3	5**
Males	8	33	1	3
Females	6	17	2	6
Headache	14	23	5	8*
Males	5	21	1	3
Females	9	25	4	12
Mental symptoms ^a	6	10	0	0*
Males	1	4	0	0
Females	5	14	0	0

Note. Differences between prevalences were obtained using a χ^2 -test.
^aDepression, anxiety.
 * $p < .05$.
 ** $p < .01$.
 *** $p < .001$.

85) and 16 children (9 boys and 7 girls; mean age = 7 years and range = 1 to 15). The respondents were asked to describe the symptoms they had experienced during the days of peak exposure, without mention of the exceptionally high emis-

sion of pollutants or what kinds of symptoms the emission may generate. Parents responded on behalf of their children.

An identical questionnaire was distributed to the same households 4 months later. The link of this reference question-

naire to the first inquiry was not revealed. The response rate was 79%, no data had to be excluded, and 66 persons were included in the analyses. The effect of confounding was controlled by studying the intraindividual difference in the symptoms in the subpopulation of 45 subjects who responded to both questionnaires. The statistical significance of the difference in the occurrence of the symptoms during the high-exposure and reference periods was assessed by a χ^2 -test and McNemar's test.²

Results

The unadjusted prevalences of the different symptoms in the two population samples are given in Table 1. Large proportions of the participants reported breathlessness (35%) and mental symptoms (10%) during the high-exposure period, while no such symptoms were indicated during the reference period. The prevalence of eye symptoms (22% vs 2%), cough or pharyngeal irritation (15% vs 5%), and nausea (14% vs 3%) were also significantly larger during the high exposure. However, nasal symptoms (8% vs 20%) were more common during the reference period than the high-exposure period, although the difference was not significant. Altogether, 63% of the subjects reported experience of at least one symptom during the high-exposure period compared with 26% during the reference period.

The presence of symptoms during the exposure and reference periods in the 45 subjects who responded to both questionnaires is shown in Table 2. Eye symptoms, cough or pharyngeal irritation, breathlessness, nausea, and headache were experienced more often during the exposure period than during the reference period. The difference was significant for breathlessness.

Discussion

The occurrence of the symptoms during the high-exposure period was large: Every third participant reported difficulties in breathing, and every fourth participant indicated irritation of eyes, headache, and nausea. Mental symptoms were also common. The prevalence of these symptoms was significantly larger than those during the reference period in the comparison of the two samples. The direction of the differences was similar in the intraindividual comparison of those who responded to both questionnaires, al-

though significance was not reached in all of the symptoms because of the smaller number of subjects than in the two-sample comparison. Interestingly, more subjects reported nasal symptoms during the reference period than during the high-exposure period. A possible explanation is that breathing difficulties due to exposure were so prominent that attention was not paid to mild nasal symptoms. The highest 4-hour concentration of H₂S was 135 µg/m³, which is nine times higher than the guideline in Canada (15 µg/m³). There are no guidelines for ambient air H₂S in Finland.

The observed symptoms correspond to physiological effects of acute exposure of H₂S suggesting direct irritative effect on mucous membranes and eye conjunctivae, although in far smaller concentrations than described earlier.³ Previously, we have observed an increased amount of eye and nasal symptoms and cough among subjects living in the most polluted area of Imatra.⁴

According to the World Health Organization (WHO) guideline values for H₂S, the highest acceptable half-hour concentration is 7 µg/m³ for odor nuisance, along with a daily mean of 150 µg/m³ for health hazards.⁵ During the period of high exposure, the highest measured 4-hour concentration (135 µg/m³) and 24-hour averages (35 and 42 µg/m³) were well below the recommendation. These kind of emissions are rather commonplace and are al-

	Exposure Period Only, No.	Reference Period Only, No.	Both Periods, No.	No Symptoms, No.	Significance ^a	
					t	P
Eye symptoms	5	1	0	39	1.63	NS
Nasal symptoms	3	11	1	30	2.14	<.05
Cough or pharyngeal irritation	5	1	0	39	1.63	NS
Breathlessness	16	0	1	28	4.00	<.001
Nausea	6	2	1	36	1.41	NS
Headache	8	2	2	33	1.90	NS
Mental symptoms ^b	2	0	0	43	1.41	NS

Note. NS = not significant.
^aMcNemar's test of significance.
^bDepression, anxiety.

ways possible wherever wood pulp production takes place. It seems likely that the WHO guideline value of 150 µg/m³ for H₂S is too high and does not provide prevention from adverse health effects. Furthermore, the presence of other pollutants should be taken into account, because H₂S is rarely the only hazardous component of air pollution. □

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Signs and symptoms of methylmercury contamination in a First Nations community in Northwestern Ontario, Canada



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HIGHLIGHTS

- Similarities between the prevalence of complaints in Minamata and Grassy Narrows
- Similarities in neurological findings were also found.
- Quantitative sensory measurements gave similar results for impairments.
- Younger Canadians were less severely affected than older ones.
- Results suggest that subjects from Grassy Narrows had methylmercury poisoning.

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ABSTRACT

In 1970, fish caught in the English–Wabigoon River system in northwestern Ontario, Canada, were found to be contaminated with mercury coming from a chlor-alkali plant in the province. In the 1970s, patients exhibiting some of the symptoms of the Hunter–Russell syndrome (e.g. paresthesias, visual field constriction, ataxia, impaired hearing, and speech impairment) were reported by some researchers. However attempts to diagnose the patients as suffering from methylmercury poisoning proved to be controversial. In order to research the presence of methylmercury contamination, and show that the patients, through eating contaminated fish, were suffering from methylmercury poisoning, we studied the results of subjective complaints, neurological findings, and quantitative somatosensory measurements gathered in Grassy Narrows Indian Reservation, Ontario, in March, 2010. At that time, the population of the Grassy Narrows settlement was around 900. Ninety-one residents volunteered to be examined. From them, we selected 80 people who were older than 15 years old, and divided them into two groups. Canadian Younger (CY): 36 residents who were from 16 to 45 years old. Canadian Older (CO): 44 residents who were from 46 to 76 years old. We compared them to Japanese Exposed (JE): 88 methylmercury exposed residents from the Minamata district in Japan, and Japanese Control (JC): 164 control residents from non-polluted areas in Japan. Complaints and abnormal neurological findings were more prevalent and quantitative sensory measurements were worse in the two Canadian groups and the Japanese Exposed group than in the Japanese Control group. Complaints, neurological findings and quantitative sensory measurements were similar in Canadian Older and Japanese Exposed. The results for Canadian Younger fell between those of Canadian Older and Japanese Control. These findings indicate that the clinical signs and symptoms of the residents of Grassy Narrows are almost the same as those recorded for Minamata disease in Japan.

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1. Introduction

Since the 1960s, a chlor-alkali plant had been releasing waste products contaminated with mercury into the waters of the English–Wabigoon River system in northwestern Ontario, Canada. In the first examples of fish, from the river system, that were contaminated with methylmercury (Bligh, 1970) levels of up to 16 µg/g were reported. Fimreite and Reynolds (1973) found highly contaminated fish with a maximum

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methylmercury concentration of 27.8 µg/g in 1970. The contamination in fish there was almost equal to that measured in fish from Minamata Bay, Japan, where a barracuda was recorded as having 23 µg/g in May 1961 (Fujiki and Irukayama, 1979). The average mercury concentrations, measured in 1971, in walleye and northern pike from Ball Lake, English–Wabigoon River, were 1.99 µg/g and 5.05 µg/g respectively (Armstrong and Scott, 1979).

In 2003, results of similar measurements were 0.40 µg/g in walleye and 0.85 µg/g in northern pike (Kinghorn et al., 2007). The concentrations of mercury in fish are declining, but they are still higher than those found in fish in Minamata Bay, Japan, where the average concentration of mercury in fish has been from 0.17 to 0.42 µg/g during the period of 1998–2004. (Kindaichi and Matsuyama, 2005). Residents living in that area of Japan, still continue to be exposed to low levels of mercury from the eating of locally caught fish.

The two First Nations' communities living in Grassy Narrows and Whitedog Indian Reservations became victims of methylmercury poisoning through the consumption of locally caught fish. Patients with some of the Hunter–Russell syndrome symptoms have been reported in these reserves (Harada et al., 1976). Canadian researchers also examined the indigenous residents of the areas. Wheatley et al. (1979) reported that effects associated with methylmercury poisoning were observed, but they concluded that direct impacts on human health were difficult to prove.

Pathological studies of a cat from Whitedog, which exhibited acute neurological symptoms, revealed high mercury levels in the brain similar to those of Minamata disease in Japan (Takeuchi et al., 1977). Another cat from neighboring Grassy Narrows showed no symptoms, but on closer examination it was shown to have high mercury levels in the brain and latent defects caused by methylmercury poisoning (Takeuchi et al., 1977).

Since 2004, more than 60,000 people from the Minamata district have been diagnosed with abnormal neurological symptoms. In many cases, the abnormalities were being reported for the first time since the release of methylmercury contaminated wastewater was stopped in 1968 (Takaoka et al., 2009). In chronic methylmercury poisoning the somatosensory disturbance from cortical damage is specific and sensory disturbance is present either in all four limbs or throughout the body, sometimes with the exception of the face and head. To detect such abnormalities, quantitative sensory measurements are useful (Takaoka et al., 2008). So we carried out a health survey that included the examination of subjective complaints, neurological symptoms, and quantitative sensory measurements in Grassy Narrows, Ontario, Canada, in 2010 and tried to reassess the effect of methylmercury in this area.

2. Materials and methods

2.1. Subjects

The study was carried out in March 2010 in Grassy Narrows, Ontario, Canada. We contacted a Grassy Narrows support group and asked for their help. They informed the indigenous population of our coming survey to detect any health effects from methylmercury poisoning and asked for volunteers to take part in the study. The Chief of Grassy Narrows First Nation went on the local radio to ask for volunteers for our research. Posters, informing of our coming research project and our wish for volunteers, were displayed in the band office and a local store. Of the approximately 900 residents, 91 volunteered to be examined. We selected 80 residents, who were older than 15, for the study. Subjects were informed verbally and in writing about the examination method, how the data would be used and that their confidentiality would be protected. Each participant gave their written consent.

We divided them into two groups. (1) Group Canadian Younger (CY): consisted of 36 residents who were from 16 to 45 years old (M/F = 18/18, 34.4 ± 9.5 years old). (2) Group Canadian Older

(CO): consisted of 44 residents who were from 46 to 76 years old (M/F = 19/25, 57.5 ± 8.1 years old).

We studied subjective symptoms, neurological findings and carried out four quantitative sensory measurements (including minimal tactile sensation, vibration, position sense, and two-point discrimination) among the 80 residents. In order to assess the state of health of the residents of Grassy Narrows, we compared them to a group of Japanese residents who had also been exposed to methylmercury as well as a group of Japanese control residents. These residents were the same people we had used as subjects in our previous study (Takaoka et al., 2008).

(3) Group Japanese Exposed (JE): was comprised of 88 randomly selected Japanese subjects. They were chosen from residents of the Minamata area who had been exposed to methylmercury and who had been included in our former study at the Minamata Kyoritsu Hospital and the Kyoritsu Neurology and Rehabilitation Clinic between November 2004 and April 2005. Their ages matched those of the corresponding Canadian group but the genders could not be matched exactly (M/F = 38/50, 59.0 ± 7.5). They answered a detailed questionnaire and were given a neurological examination including the same four quantitative sensory measurements as we performed in Canada. All of them were born before 1969. In our former study, we separated the subjects into those with and without neurological or neurologically related diseases, but we found that there was little difference between those two groups. So in this study, Group JE included subjects both with and without such related diseases.

(4) Group Japanese Control (JC): consisted of 164 residents who lived in other districts, e.g. around Fukuoka City, Kumamoto City, and Kagoshima City, aged between 40 and 79. In the control group, people who had lived around Minamata City or who suffered from a neurological disease or a neurologically related illness were excluded. The control subjects were examined between February and May 2006 (M/F = 67/97, 58.4 ± 11.6).

2.2. Epidemiological conditions and questionnaire on complications

The questionnaire, both in Canada and Japan, included questions to determine the subject's exposure to methylmercury and asked for information regarding place of residence, dietary habits, occupational history, medical complications and the health and medical histories of family members.

The questionnaire on complaints for the Canadian groups (CO and CY) consisted of 47 questions related to sensory impairment (7 items), somatic pain (4), visual impairment (3), hearing impairment (3), tasting and smelling problems (3), in-coordination of the extremities (4), other movement impairment (11), vertigo and dizziness (4), general complaints (2), and mental and intellectual problems (6).

The questionnaire on complaints for the Japanese groups (JE and JC) consisted of about 50 questions. We selected 35 relevant questions from the Japanese questionnaire and used them in the Canadian one. They were as follows: sensory impairment (4 items), somatic pain (3), visual impairment (3), hearing impairment (3), tasting and smelling problems (3), in-coordination of the extremities (5), other movement impairment (4), vertigo and dizziness (4), general complaints (2), and mental and intellectual problems (4).

In answer to questions on health complaints, subjects were asked to select one of 4 possible choices. 1) Yes, always, 2) Yes, sometimes, 3) Yes, in the past but not at present, and 4) No, never. The prevalence of each complaint was calculated for each group and then compared between the four groups. All subjects completed the questionnaire before their medical examination. Subjects who could not complete the questionnaire by themselves were asked the questions verbally. All questionnaires were reviewed prior to the examinations.

2.3. Standard neurological examination

A standard neurological examination was carried out on 32 of the 36 subjects in Group CY and on all 44 subjects in Group CO. Dysarthria, auditory disturbance, visual constriction, finger–nose test with the eyes open and closed, diadochokinesis, heel–shin test, gait disturbances, tandem gait test, Mann's test, balancing on one foot with eyes open and closed, and superficial sensory disturbance (touch and pain) were used and tested for. The examination methods and criteria were almost the same as the former study (Takaoka et al., 2008).

Dysarthria, auditory disturbance, visual constriction, postural hand tremors, gait disturbances and Romberg's sign were judged to be either present or absent. Dysarthria, auditory disturbance, and visual field constriction were judged by the examining physician without using special instruments. Tunnel vision was considered to be present when the confrontation test showed a lateral field of vision of 80° or less.

Limb and truncal ataxia were judged as being either absent, mildly abnormal or moderately to severely abnormal. The results of the finger–nose test and the heel–shin test were judged to be positive not only when there was constant dysmetria or decomposition but also when there was uncertain dysmetria, decomposition, or very slow movement involved. Dysdiadochokinesis was judged to be present from when there was a constant abnormality to when there was an uncertain abnormality or slow movement. Tandem gait disturbance was judged as present not only when the subject could not walk more than five steps but also when they could walk five steps but were unstable. In the balancing on one foot test, disequilibrium was judged as present when it was impossible to balance more than 3 s or when the subject was unstable, but could keep their balance for more than 3 s.

The examinations were carried out in Canada by one neurologist and four psychiatrists. The neurologist and two of the psychiatrists had previous experience in carrying out these tests from earlier examinations of Minamata disease patients. The other two psychiatrists had been briefed and trained to carry out the tests. In Japan, Group JE was examined by six physicians and one neurologist and Group JC was examined by forty-five physicians, several of whom were neurologists.

Because there was not enough data collected from Group JE for the finger–nose test with eyes closed, Mann's test, Romberg's sign or balancing on one foot with eyes closed test, we excluded that information from our calculations.

2.4. Quantitative sensory measurements

Four categories of tests were used in the quantitative measurement of the somatosensory system. All four categories were the same as in the former study (Takaoka et al., 2008).

2.4.1. Assessment of minimal tactile sense

The minimal tactile sense was measured by the Semmes–Weinstein monofilament test. Twenty kinds of filaments from 0.008 to 300 g were used. Subjects were tested with eyes closed after receiving clear instructions on which locations would be tested. Each filament was pushed until it bent about 90° for about a second. The threshold was the smallest size filament which a subject could feel as touch. The trial was performed starting from a smaller size filament and then gradually increasing the size.

Each filament was tested only once except when the subject was unsure. In that case the examiner, using the same filament, repeated the test an odd number of times and selected the dominant response. If a subject could not detect the maximum filament (300 g), we defined the threshold as 400 g for calculation. Testing was carried out on the lower lip, upper chest and ventral sides of both index fingers and big toes.

2.4.2. Vibration sense

Vibration sense was measured by using a 128 Hz tuning fork. The vibration test was carried out on the middle or upper sternum, the radial side of both wrists and the fibular side of both ankles. Subjects were told to indicate when they no longer could feel the vibrations. The examiner simultaneously struck a tuning fork and started a stopwatch, then placed the base of the fork against the area to be tested. The time interval until the subject reacted was recorded.

2.4.3. Position sense

The testing of position sense was carried out on subjects with their eyes closed. A ruler with a millimeter scale was used. Tests were carried out on the subject's index fingers and big toes. A ruler was placed vertically alongside the digit. With the digit held horizontally, the zero point was the position of the digit's nail on the ruler's scale. The examiner held the digit by its sides and moved it either up or down, holding the position for about 1 s. The subject was asked to indicate whether they felt the movement and if it was up or down. The upward or downward movement started from 5 mm from the zero point and was considered to be the minimum value. The movement was increased in 5 mm increments and the subject's threshold distance was recorded.

Each trial was carried out once for each distance except when the subject was uncertain. In that case the examiner would repeat the test again for an odd number of times and choose the dominant response. If the subject could not feel the maximum movement, the threshold was defined as the maximum distance plus 5 mm.

2.4.4. Two-point discrimination

The two-point discrimination test was carried out on subjects while their eyes were closed. A drafting divider, with the legs set at different distances, was pressed against the subject's skin at an angle of 30 to 45° to a depth of between 1 and 2 mm for about 1 s. The distances between the points used in the test were 1, 2, 3, 4, 5, 6, 8, 10, 12, 15, 20, 25, 30 and 36 mm. The threshold recorded was the shortest distance at which a subject answered correctly. This method was performed on the lower lip and the ventral side of each index finger. If the subject was unable to detect the maximum distance of 36 mm, the threshold was defined as 40 mm for calculation purposes.

In testing Groups CO and CY, the “Yes/No” method was used. However, when a subject felt that 1-point stimulation was actually 2-point stimulation, they were re-tested using the “2-alternative, forced-choice method”. In Groups JE and JC the “2-alternative, forced-choice method” was used exclusively.

2.5. Statistical methods

All the calculations were performed using MS Excel and SPSS. Chi square analysis was used in MS Excel when the prevalence was compared, and t-test was used in MS Excel when the average was compared. The correlations were calculated by SPSS.

When we calculated the minimal tactile sense, we converted the grams to the evaluator size using the equation: Evaluator size = $\log([\text{gram}]) + 4$.

3. Results

3.1. The subjects' backgrounds

The age and sex of the subjects are shown in Table 1. The age and sex in Groups CO, JC and JE were not statistically different. The age of Group CY was less than the other groups.

From Table 2, we can see that 86% of Group CO and 83% of Group CY answered the question on how they obtained fish and over 60% of Groups CO and CY answered that they are catching fish by themselves. Also from Table 2, we can see that 41% of Group JE and 1% of Group JC

Table 1

Age and sex of each group.

	Age	n (M/F)
Group CO	57.5 ± 8.1	44 (19/25)
Group CY	34.4 ± 9.5	36 (18/18)
Group JE	59.0 ± 7.5	88 (38/50)
Group JC	58.4 ± 11.6	164 (67/97)

belonged to a fisher family. Ninety-three percent of Group JE and 25% of Group JC ate fish every day.

Table 3 shows the relevant medical history of Group CO and Group CY. The information was collected through interviews. On the question of hypertension, although some subjects had no recorded history of hypertension, high blood pressure was detected during the tests. If we detected a systolic pressure of 170 or more or and diastolic pressure of 110 or more in a subject, we recorded that hypertension was present. Some neurological or neurologically related diseases were found in 47 subjects (53%) of Group JE. No neurological or neurologically related diseases were found in Group JC.

3.2. Questionnaire on medical complaints

Medical complaints reported from each group are shown in Table 4, and the p-values by chi square among the four groups are shown in Table 5. In general, the prevalence in both “Yes, always” and “Yes, always” + “Yes, sometimes” in Groups JE, CO, and CY was statistically higher than Group JC. In general, the prevalence in Group JE and Group CO was similar. For most of the complaints Group CY showed a lower prevalence than Group CO.

The questionnaire consisted of questions related to specific and non-specific symptoms in the methylmercury polluted area. Specific symptoms included numbness, difficulty in speaking, fine-finger tasks, buttoning, losing slippers while walking, difficulty in differentiating tastes, detecting smells etc. Non-specific symptoms included headaches, forgetfulness, general fatigue, and so on. In specific symptoms, the prevalence of the answer “Yes, always” + “Yes, sometimes” was lower in Table 4. A tendency to a similar prevalence was observed both in specific and non-specific symptoms.

The correlation efficient among four groups was shown in Table 7. In “Yes, always” answers, the correlation between Groups JE and CO was highest, and was followed by the one between Groups CO and CY. In “Yes, always” + “Yes, sometimes” answers the correlation between Groups CO and CY was highest, and was followed by the one between Groups JE and CO and between Groups JE and CY.

Table 2

Fish sources and frequency of ingestion.

In Canada	Group CO	Group CY
Self-caught fish	28/44 (64%)	24/36 (67%)
Fish caught by relatives and friends, purchased etc.	30/44 (68%)	22/36 (61%)
A combination of both the above	38/44 (86%)	30/36 (83%)
In Japan	Group JE	Group JC
Fishermen	10/88 (11%)	0/164 (0%)
Fishermen's families	36/88 (41%)	1/164 (1%)
Sport fishing/recreational fishing	62/88 (70%)	17/161 (11%) ^b
Daily ingestion	81/87 (93%) ^a	40/157 (25%) ^c
Ingestion more than once a week	85/87 (98%) ^a	119/157 (76%) ^c

^a Datum for 1 person was missing.

^b Data for 3 persons were missing.

^c Data for 7 persons were missing.

Table 3

Complications in Canadian subjects.

	Group CO	Group CY
Hypertension	15 (34%)	16 (44%)
Diabetes mellitus	8 (18%)	3 (8%)
Stroke	3 (7%)	1 (3%)
Lung diseases	0 (0%)	1 (3%)
Stomach diseases	6 (14%)	1 (3%)
Heart diseases	1 (2%)	0 (0%)
Orthopedic diseases	7 (16%)	4 (11%)
Psychiatric diseases	3 (7%)	1 (3%)

3.3. Neurological examination

The neurological findings for each group and p-values by chi-square among the four groups are shown in Table 6. The prevalence was generally highest in Group JE, and the prevalence of all the findings of Groups JE and CO was statistically higher than Group JC. All the findings of Group CY were less prevalent than Group CO, and seven of twelve findings of Group CO showed statistically higher prevalence than Group CY.

The most prevalent findings in Groups CO are tandem gait abnormality and somatosensory disturbances of pain and touch, followed by hearing impairment, truncal ataxia other than tandem gait abnormality, upper extremity ataxia (finger–nose test and diadochokinesis), and lower extremity ataxia (heel–shin test). The prevalence of visual constriction or dysarthria was lower. Although the orders of prevalence for the positive findings were different, the tendencies of the abnormalities were similar between Groups CO and JE.

Correlation among four groups was shown in Table 7. Correlations between Groups JE and CY, Groups CO and CY, and Groups JE and CO were higher than those between Group JC and other three groups, and p-values were lower.

3.4. Quantitative sensory measurements

3.4.1. Minimal tactile sensitivity using the Semmes–Weinstein monofilament test

Thirty-three subjects (75%) of Group CO and 24 subjects (67%) of Group CY were examined. One set of data for the lower lip in Group CO and one set of data for the left and right big toes in Group CY were absent. 84 of 88 subjects (95%) in Group JE (in which three sets of data were missing for the lower lip) and all 164 subjects of Group JC were examined and calculated.

Fig. 1 shows the results of the minimal tactile sensitivity using the Semmes–Weinstein monofilament test. The results were worst in Group CO, and there were distinct statistical differences between Groups CO, CY, and JC. Group JE was, in general, positioned between Groups CO and CY.

3.4.2. Vibration sense

Thirty-five subjects from Group CO and 25 subjects from Group CY were examined. Two subjects from Group CO and one subject from Group CY were unable to carry out the test correctly and were excluded from the results. Consequently, the results of 33 subjects (75%) from Group CO and 24 subjects (67%) from Group CY were used in the calculation. Three sets of data for the right ankle and 4 sets of data for the left ankle were absent for Group CO. All 88 subjects of Group JE and all 164 subjects of Group JC (in which one set of data for the chest and one set of data for the left and right ankles were absent) were examined and calculated.

Fig. 2 shows that the vibration sense was worst in Group JE, followed by Group CO, Group CY and Group JC. Most of them had statistical differences between each other.

Table 4
Percentage of complaints.

		Yes, always				Yes, always + Yes, sometimes			
		Group CO	Group CY	Group JE	Group JC	Group CO	Group CY	Group JE	Group JC
1	Numbness in hands	40%	11%	49%	2%	86%	75%	92%	6%
2	Numbness in legs	39%	8%	42%	1%	91%	61%	86%	6%
3	Cannot judge bath water temperature	26%	8%	15%	0%	47%	31%	35%	0%
4	No pain when burned or wounded	23%	17%	16%	0%	65%	49%	44%	0%
5	Hand weakness	34%	22%	56%	3%	78%	69%	81%	5%
6	Leg weakness	35%	11%	49%	2%	79%	54%	77%	4%
7	Tremor in hand	23%	19%	24%	2%	74%	67%	68%	4%
8	Difficulty in speaking	2%	6%	8%	0%	51%	53%	62%	2%
9	Difficulty in fine finger tasks	47%	14%	57%	0%	77%	72%	86%	7%
10	Dropping things	9%	8%	16%	0%	77%	47%	73%	6%
11	Difficulty in buttoning clothes	21%	6%	25%	0%	49%	28%	57%	0%
12	Stumbling	29%	17%	5%	0%	79%	58%	65%	1%
13	Losing slippers while walking	8%	0%	23%	0%	50%	27%	70%	1%
14	Disturbed vision	33%	19%	49%	3%	93%	75%	87%	15%
15	Difficulty in finding things in shops	13%	9%	29%	0%	63%	46%	72%	6%
16	Limited peripheral vision	32%	14%	25%	1%	59%	31%	64%	4%
17	Difficulty in hearing	42%	25%	35%	7%	72%	61%	71%	15%
18	Tinnitus	30%	19%	34%	6%	86%	81%	80%	17%
19	Can hear, but cannot understand	5%	3%	7%	1%	65%	64%	45%	6%
20	Difficulty in differentiating tastes	28%	6%	18%	0%	53%	28%	46%	1%
21	Difficulty in sampling food while cooking	26%	0%	15%	1%	48%	23%	47%	1%
22	Difficulty in detecting smells	28%	11%	22%	0%	49%	28%	48%	4%
23	Muscle cramps	33%	17%	31%	3%	98%	91%	91%	29%
24	Headaches	37%	25%	37%	1%	88%	81%	86%	30%
25	Shoulder stiffness	24%	6%	64%	10%	95%	53%	95%	51%
26	Forgetfulness	21%	17%	34%	1%	81%	72%	97%	52%
27	Inability to hold concentration at work	26%	3%	28%	0%	74%	58%	67%	11%
28	Lack of motivation to do things	16%	0%	26%	1%	58%	56%	86%	21%
29	Irritation	21%	22%	31%	0%	72%	78%	85%	33%
30	Difficulty in sleeping	37%	39%	39%	3%	74%	69%	84%	19%
31	Dizziness when standing up	23%	14%	15%	0%	86%	83%	85%	17%
32	Feeling of head spinning	0%	3%	3%	1%	49%	58%	63%	5%
33	Swaying dizziness	5%	3%	5%	1%	72%	72%	57%	6%
34	Dizziness, bordering on fainting	7%	0%	5%	1%	47%	22%	46%	2%
35	General fatigue	40%	31%	45%	2%	95%	78%	87%	25%

3.4.3. Position sense

Twenty-eight subjects from Group CO and 24 subjects from Group CY were examined. One subject from Group CO and one subject from Group CY were unable to carry out the test correctly and were excluded from the results. Consequently, the results of 27 subjects (61%) from Group CO and 23 subjects (64%) from Group CY were used in the calculation. One set of data for the left and the right big toe, both upward and downward movements, was absent for Group CO. Eighty-seven subjects from Group JE (in which one set of data for both big toes in both directions was absent) and all 164 subjects of Group JC were examined and calculated.

Fig. 3 shows that the position sense was worst in Group JE, followed by Group CO, Group CY, and Group JC. Although there were some exceptions, most of the groups had statistical differences.

3.4.4. Two-point discrimination

Thirty-four subjects from Group CO and 25 subjects from Group CY were examined. Two subjects from Group CO and one subject from Group CY were unable to carry out the test correctly and were excluded from the results. Consequently, the results of 32 subjects (73%) from Group CO and 24 subjects (67%) from Group CY were used in the calculation. 87 of 88 subjects (99%) from Group JE and all 164 subjects of Group JC (in which one set of data for the right index finger was absent) were examined and calculated.

Fig. 4 shows that the position sense was worst in Group JE or Group CO, followed by Group CY and finally Group JC. Most of them had statistical differences, except for the results for index fingers when comparing Group JE with Group CO.

Table 5
p-Value for complaints – comparing groups.

		p < 0.01	p < 0.05	n.s.
“Yes, always”	CO, JC	All others	Nos. 25, 34	Nos. 8, 19, 32, 33
	CY, JC	All others	Nos. 1, 2, 6, 8, 11, 18, 20	Nos. 13, 19, 21, 25, 27, 28, 32, 33, 34
	JE, JC	All others	Nos. 12, 19	Nos. 32, 33, 34
	CO, CY	Nos. 1, 2, 9, 21	Nos. 6, 20, 27, 28	All others
	JE, CO	Nos. 12, 25	No. 5	All others
	JE, CY	Nos. 1, 2, 5, 6, 9, 13, 14, 25, 27, 28	Nos. 11, 15, 21	All others
“Yes, always” + “Yes, sometimes”	CO, JC	All	–	–
	CY, JC	All others	No. 26	No. 25
	JE, JC	All	–	–
	CO, CY	Nos. 2, 25	Nos. 6, 10, 16, 20, 21, 34, 35	All others
	JE, CO	No. 28	Nos. 4, 19, 26	All others
	JE, CY	Nos. 2, 11, 13, 16, 25, 26, 28	Nos. 1, 6, 10, 15, 21, 34	All others

Table 6
Neurological findings and group comparisons.

Examination	Prevalence of abnormality				p-Value						
	Group CO	Group CY	Group JE	Group JC	CO, JC	CY, JC	JE, JC	CO, CY	JE, CO	JE, CY	
Hearing impairment	49%	17%	32%	6%	<0.01	n.s.	<0.01	<0.05	n.s.	n.s.	
Visual constriction	14%	0%	28%	0%	<0.01	n.s.	<0.01	n.s.	n.s.	<0.01	
Dysarthria	17%	3%	18%	1%	<0.01	n.s.	<0.01	n.s.	n.s.	n.s.	
Postural tremor	20%	19%	28%	3%	<0.01	<0.01	<0.01	n.s.	n.s.	n.s.	
Normal gait–unstable	28%	6%	30%	5%	<0.01	n.s.	<0.01	<0.05	n.s.	<0.05	
Tandem gait–unstable	87%	34%	68%	7%	<0.01	<0.01	<0.01	<0.01	<0.05	<0.01	
Finger–nose test (eyes open)	21%	0%	47%	0%	<0.01	n.s.	<0.01	<0.05	<0.01	<0.01	
Adiadokokinesis	23%	3%	43%	1%	<0.01	n.s.	<0.01	<0.05	n.s.	<0.01	
Balancing on one foot (eyes open)	53%	22%	63%	8%	<0.01	<0.05	<0.01	<0.05	n.s.	<0.01	
Heel–knee test	24%	0%	50%	1%	<0.01	n.s.	<0.01	<0.05	<0.05	<0.01	
Touch disturbance (four limbs)	50%	44%	83%	1%	<0.01	<0.01	<0.01	n.s.	<0.01	<0.01	
Pain disturbance (four limbs)	59%	50%	97%	1%	<0.01	<0.01	<0.01	n.s.	<0.01	<0.01	

4. Discussion

Our results show that subjective complaints were most prevalent in Group JE, followed by Groups CO, CY and JC. Similar and high prevalence of more specific complaints from methylmercury poisoning between Groups JE and CO suggest that these similarities are mainly related to methylmercury poisoning. The increase of non-specific complaints, which was found in Group JE, was also observed in Group CO.

The high prevalence of somatosensory disturbance and following ataxic movement in Groups JE and CO suggests that those two groups are similarly affected by methylmercury and Group CY is affected to a smaller extent by methylmercury. Harada et al. (1976) conducted health surveys on 89 indigenous inhabitants of Grassy Narrows and Whitedog and found sensory disturbance (47.6%), abnormality in visual field (18.0%), impaired hearing (44.9%), ataxia (9.0%), and dysarthria (5.6%). These findings together with the Hunter–Russell syndrome suggest methylmercury pollution in these communities.

Except for the high prevalence of tandem gait abnormality and hearing loss, the pattern of prevalence is almost the same as our study from the Minamata area in the 1970s (Fujino, 1994). Harada and his colleague visited Grassy Narrows in 2002 (Harada et al., 2005a) and Grassy Narrows and Whitedog in 2004 (Harada et al., 2005b). In 2002, glove and stocking type of sensory disturbance (54.4%), tunnel vision (10.5%), ataxia (12.3%) and impaired speech (12.3%) were observed in 57 subjects (Harada et al., 2005a). Combining the results of both studies, 2002 and 2004, glove and stocking type sensory disturbance was found in 65.1% of the cases, tunnel vision in 10.8%, ataxia in 25.1% and impaired speech in 6.9% of the 175 subjects (Harada et al., 2005b). As the criteria used for determining ataxia was not described in those papers, it is possible that the actual percentage could be greater than the papers suggested. We show the raw data for ataxic movement in this study.

Our present study differs from the former studies of 1975, 2002 and 2004, in that quantitative measurements of somatosensory disturbance were added to the study. The results of two-point discrimination sensitivity of the lower lip, vibration sense and position sense in big toes were also worse in Group JE, followed by Groups CO, CY and JC. Somatosensory acuity was most impaired in Group JE. Whereas

minimal tactile sensitivity of the lower lip and left big toe were worst in Group CO, followed by Groups JE, CY and JC. The reason for these differences is, as yet, unascertained. As to two-point discrimination, the “Yes/No” method was used in testing Groups CO and CY, and the “2-alternative, forced-choice method” was used in testing of Groups JE and JC. But, in our experience, there were no great differences between results of these two methods.

Quantitative measurements showed that somatosensory disturbance, showing a similar pattern, was present in all tested body areas. These patterns are assumed to be the characteristics of somatosensory disturbance due to a uniformly injured central nervous system, especially the sensory cortex.

The similarity in the symptoms of abnormalities, neurological findings and quantitative measurements in Groups JE and CO were assumed to be produced by methylmercury poisoning. The intermediate abnormalities in Group CY suggest a milder and continuing effect of methylmercury poisoning in the younger generations of this area.

There are some limitations in this study. The first one is that the subjects in the study consisted of applicants who volunteered for the examination. The subjects in Groups JE, CO and CY ate a lot of fish, but the subjects in Group JC ate less fish. Also the lifestyle and occupations of the Japanese and the Canadian subjects are likely to be quite different. Also, the lifestyle and occupations were not the same in the two Japanese groups JE and JC.

Secondly we had no control area in Canada. Instead, we compared the Canadian results with the results from a control area in Japan, as well as from an exposed area in Japan.

Thirdly, there can be other factors involved which can affect the findings. In Groups CO and CY, some neurological diseases were found which confused the analysis of the test results. In order to overcome this limitation, we tried to compare a wide range of symptoms and complaints, neurological findings and quantitative measurements.

In the earlier study in Japan, we found that some complaints, symptoms, neurological findings, and quantitative measurements recorded could be affected by the presence of certain other neurological diseases. However, the similar patterns of symptoms, neurological findings, and quantitative sensory measurements cannot be explained without taking

Table 7
Correlation of prevalence of complaints and neurological examinations – group comparisons.

		CO, JC	CY, JC	JE, JC	CO, CY	JE, CO	JE, CY
“Yes, always”	Correlation coefficient	0.315	0.301	0.549	0.630	0.712	0.450
	p-Value	n.s.	n.s.	<0.01	<0.01	<0.01	<0.01
“Yes, always” + “Yes, sometimes”	Correlation coefficient	0.578	0.521	0.693	0.813	0.787	0.712
	p-Value	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Neurological examination	Correlation coefficient	0.628	0.242	0.048	0.784	0.708	0.825
	p-Value	<0.05	n.s.	n.s.	<0.01	<0.01	<0.01

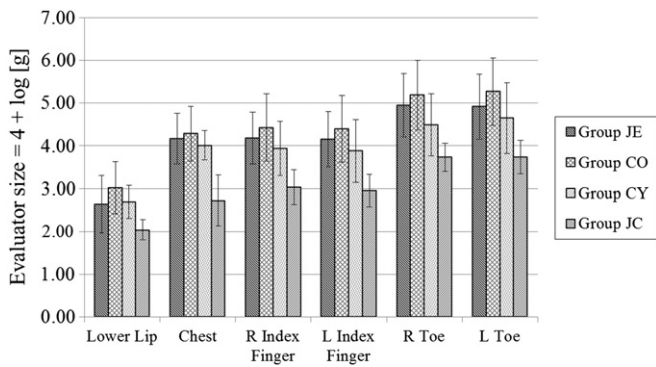


Fig. 1. Threshold for minimal tactile sense – group comparisons. JC, JE: $p < 0.01$ (all locations), JC, CO: $p < 0.01$ (all locations), JC, CY: $p < 0.01$ (all locations), JE, CO: $p < 0.01$ (lower lip), $p < 0.05$ (L toe), n.s. (other locations), JE, CY: $p < 0.01$ (R toe), $p < 0.05$ (chest and R index finger), n.s. (other locations), and CO, CY: $p < 0.05$ (chest), $p < 0.01$ (other locations).

into account the possibility of the presence of methylmercury poisoning (Takaoka et al., 2008).

After Harada's paper in 1976, the health effects of methylmercury on indigenous Canadians (First Nations) were reported by Canadian researchers. Barbeau et al. (1976) reported that he discovered symptoms like Minamata disease patients in Quebec, but he soon modified and toned down his conclusions. Shephard (1979) admitted the higher exposure in Canadian Indians and insisted that there was no agreement on the clinical diagnosis of mercury poisoning. But no conclusive human health-related data of Canadian Indians were presented by them. Wheatley et al. (1979) reported that they failed to prove abnormalities attributable to methylmercury. But his study in 1979 was based on clinical and pathological test results taken from only one male Cree Indian.

In north-western Quebec, McKeown-Eyssen and Ruedy (1983) studied individuals from the Cree First Nation and reported incoordination (15.4% in males/6.5% in females in Mistassini, 44.2% in males/26.5% in females in Great Whale), abnormal perception of sensations (5.7% in males/4.3% in females in Mistassini, 9.3% in males/2.1% in females in Great Whale). The results for subjects who had visual field scores of over 55° were 16.0% in males and 19.4% in females in Mistassini, and 0.7% in males and 15.5% in females in Great Whale. Although the patterns of abnormalities are very different from our results, the presence of these abnormalities could suggest milder methylmercury poisoning. The Canadian researchers did not, however, come to this conclusion. It would appear that they did not follow up and observe the individuals for a longer period of time, which is unfortunate. In our new Minamata disease cases, observed from November 2004 to April 2005, about half

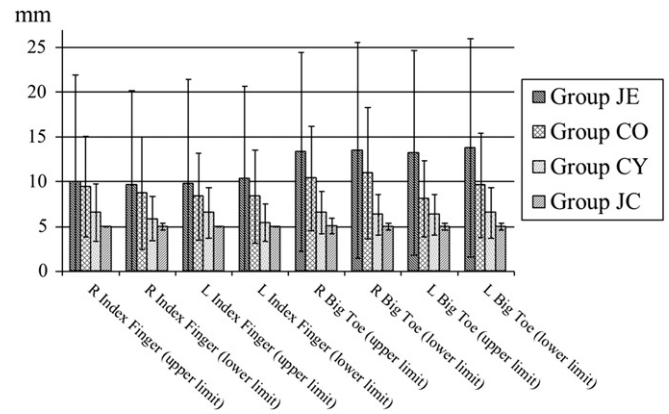


Fig. 3. Threshold for position sense – group comparisons. JC, JE: $p < 0.01$ (all locations), JC, CO: $p < 0.01$ (all locations), JC, CY: $p < 0.05$ (R index finger–lower), n.s. (L index finger–lower), $p < 0.01$ (all other locations), JE, CO: $p < 0.01$ (L big toe–upper & lower), $p < 0.05$ (R big toe–upper), n.s. (all other locations), JE, CY: $p < 0.05$ (L index finger–upper), $p < 0.01$ (all other locations), and CO, CY: $p < 0.05$ (R index finger–lower, L index finger–upper, L big toe–upper), $p < 0.01$ (all other locations).

of them were considered to have had their first abnormalities after 1968, the year when the Chisso Company ceased to release methylmercury contaminated industrial wastewater (Takaoka et al., 2009).

Spitzer et al. (1988) found no abnormalities in north-western Quebec when they compared people from the Cree First Nation with a control group. In this study, the exposed group (SDD: The Self Designated Disease Group) and other three control groups were compared. Visual constriction was observed in 4.9% of SDD and in 0.0–1.7% of other groups. Peripheral sensory disturbance (written as “peripheral neuropathy” in the paper) was observed in 9.9% of SDD and in 1.5–3.1% of other groups. There was a higher tendency in the prevalence in SDD, but there was no statistical difference between SDD and other groups.

In examining the Cree people, McKeown-Eyssen et al. (1990) emphasized inter-observer variation. It is more important, however, to do the same examination in the control area and to set criteria for judging the results of the examination, rather than to repeat an examination in the same group. Even though there were some variations and differences between the results obtained by the screener and the results of the neurological examination by the neurologist, e.g. prevalence of tremor (screener 40.2%, neurologist 29.9%) and incoordination (screener 22.8%, neurologist 15.4%) in men in Mistassini, they were still high. They also had differences in criteria when identifying neurological abnormalities, but it should be possible to set standard criteria for the assessment of the neurological findings similar to our methods.

Changeability of neurological functions is quite common in cases of Minamata disease. In Minamata disease the range of four limb

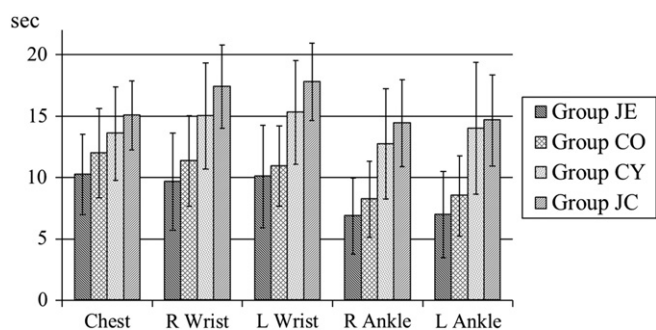


Fig. 2. Threshold for vibration sense – group comparisons. JC, JE: $p < 0.01$ (all locations), JC, CO: $p < 0.01$ (all locations), JC, CY: $p < 0.01$ (bilateral wrist), $p < 0.05$ (chest and R ankle), n.s. (L ankle), JE, CO: $p < 0.01$ (chest), n.s. (L wrist), $p < 0.05$ (other locations), JE, CY: $p < 0.01$ (all locations), and CO, CY: n.s. (chest), $p < 0.01$ (all other locations).

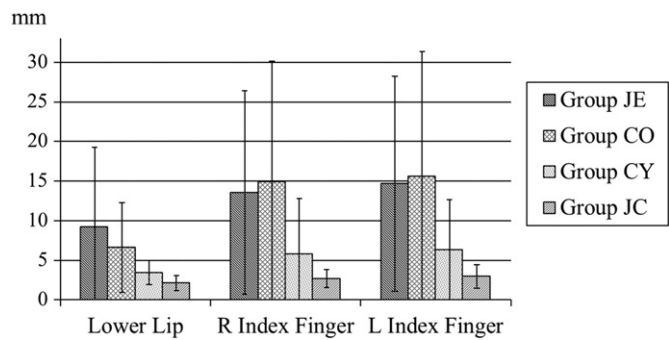


Fig. 4. Threshold for two-point discrimination – group comparisons. JC, JE: $p < 0.01$ (all locations), JC, CO: $p < 0.01$ (all locations), JC, CY: $p < 0.05$ (R index finger), $p < 0.01$ (other locations), JE, CO: $p < 0.05$ (lower lip), n.s. (other locations), JE, CY: $p < 0.01$ (all locations), and CO, CY: $p < 0.01$ (all locations).

somatosensory disturbance is changeable. Uchino and Araki (1984) reported on 100 cases of Minamata disease. In 77 of the 100 cases the examination for superficial sensory disturbance was carried out from 2 to 5 times, and 63 of the 77 cases (82%) were recorded as “unstable type” in which the area of the body showing somatosensory disturbance changed. The most important factor in showing the effect of environmental pollution on the inhabitants of an area is the ability to gather data and information from both the people exposed to the pollution and from a control group which has not been exposed.

There are some other Canadian studies about the exposure to methylmercury (Wheatley and Paradis, 1996; Wheatley et al., 1997; Wheatley and Paradis, 1998), but there are few that take into account epidemiological human health data. Wheatley (1996) stressed that the people of the First Nations understanding of mercury contamination is influenced by their holistic concepts of health and environment. But there was too little physical data available to corroborate this concept. Without the presence of human physical data, we cannot evaluate psychological, social and spiritual values of health.

5. Conclusions

The data collected from methylmercury-exposed indigenous residents of Grassy Narrows suggest that they were poisoned by methylmercury. The health abnormalities also appear to exist in a milder form in the younger generations from Grassy Narrows.

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Conflict of interest

There is no conflict of interest in this study.

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