

# 100 Years of Sediment Accumulation History of Organic Halogens and Heavy Metals in Recipient and Nonrecipient Lakes of Pulp Industry in Finland

MIKA A. KÄHKÖNEN,<sup>\*,†</sup>  
KIMMO P. SUOMINEN,<sup>†</sup>  
PENTTI K. G. MANNINEN,<sup>‡</sup> AND  
MIRJA S. SALKINOJA-SALONEN<sup>†</sup>

University of Helsinki, Department of Applied Chemistry and Microbiology, Biocenter, P.O. Box 56, 00014, Finland, and Lahti Research Laboratory, Niemenkatu 73 C, 15210 Lahti, Finland

Rate of sediment accumulation of extractable organic halogen (EOX) and of 12 trace elements (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, V, and Zn) were analyzed retrospectively over 100 years in the recipient area of pulp mills in Lake Saimaa and in two nonrecipient forest lakes in south-eastern Finland. The sediments were dated by <sup>210</sup>Pb and <sup>137</sup>Cs activities. From 1880s to 1940s, <1 mg of EOX-Cl accumulated m<sup>-2</sup> year<sup>-1</sup> in the sediment of southeastern Lake Saimaa, but accumulation increased to 1350 mg of EOX-Cl m<sup>-2</sup> year<sup>-1</sup> from the 1950s to the 1980s at 3 km and to 500 mg at 5 km from the discharge point of bleaching pulp mills. Abandoning elemental chlorine in bleaching and adopting biological treatment for wastewaters in the 1990s associated with a decreasing the sediment accumulation of EOX to <400 mg of EOX-Cl m<sup>-2</sup> year<sup>-1</sup> at both sites. The deposition rates of inorganic elements were similar in all three lakes from 1880s to 1940s, 5–40 mg m<sup>-2</sup> year<sup>-1</sup> for Mn and Zn, 1–5 mg m<sup>-2</sup> year<sup>-1</sup> for Cr, Cu, Ni, Pb, Sn, and V, and below 1 mg m<sup>-2</sup> year<sup>-1</sup> for As, Cd, Co, and Hg. After the 1950s, the sediment accumulation rates of Cd, Cr, Cu, Hg, Ni, Pb, Sn, Zn, and carbon increased 2–5-fold in the recipient lake and those of Pb, Hg, and Sn also in the nonrecipient lakes. From each ton of adsorbable organic halogen (AOX) discharged by the mills, 0.6–0.1 mg of EOX-Cl m<sup>-2</sup> accumulated in the Lake Saimaa sediments at 3–5 km from the mills. From the slope of sediment accumulation vs time, the half-life of the EOX of pulp mill origin in the sediment was estimated as 60–80 years. The rates of sediment accumulation of Hg during the decades when organomercurials were used as slimicides show that sediment was not the main sink for the Hg.

## Introduction

Sediment accumulated organic chlorine compounds and heavy metals are partly of natural origin (1–4), but large

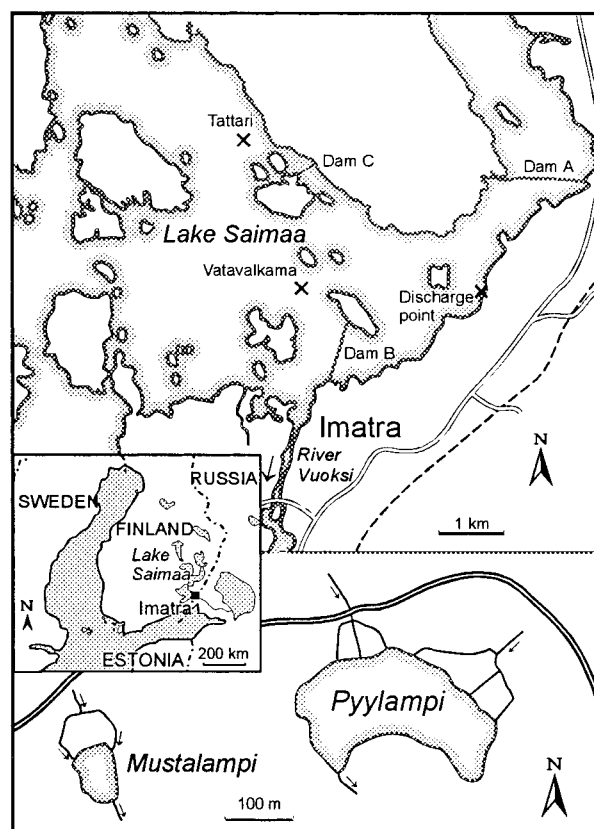


FIGURE 1. The locations of the study sites Vataavalkama and Tattari in Lake Saimaa in the pulp mill recipient area and of the nonrecipient forest lakes Pyylampi and Mustalampi 20 km NW from the mill. Dam A was constructed in 1965–1968 and Dam B 1974–1975. Dam C is submerged and was operational in 1980s and 1990s.

amounts are discharged by industry. Bleaching pulp mills in Finland have been for decades the main discharger of organic halogens. Finland produced, in 1995,  $6.1 \times 10^6$  tons of pulp and paper, of which  $5.1 \times 10^6$  tons were bleached.

Recipient sediments near pulp mills are known to accumulate high amounts of organic chlorine compounds (5–10), but little is known on their long-term fate in the anaerobic lake sediment. From the late 1980s to today, the Finnish pulp mills did large environmental investments to minimize their discharges. Elemental chlorine was abandoned, external wastewater treatment was introduced, and oil and coal as fuels were in many mills replaced by natural gas. We analyzed the sediments of recipient waters to inspect the entire pollution history, from before the industrialization to after the environment-saving operations. Knowledge on the present status of the old sediment deposits can create a basis for prognosing the future risks from the legacy of past pollution.

The sediment accumulation rates of organic halogens (EOX) and of trace elements (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, V, and Zn) were measured in the recipient area of intensive pulping industry. The sediments accumulated over 100 years during which the area changed from relative pristine to heavily industrialized pulp mill area. Since there are no large lakes that do not receive industrial effluents, small lakes from the same area that were subject to forest harvesting, but did not receive wastewaters, were used as reference.

\* Corresponding author fax: 358-9-70859322; e-mail: Mika.Kahkonen@Helsinki.fi.

<sup>†</sup> University of Helsinki.

<sup>‡</sup> Lahti Research Laboratory.

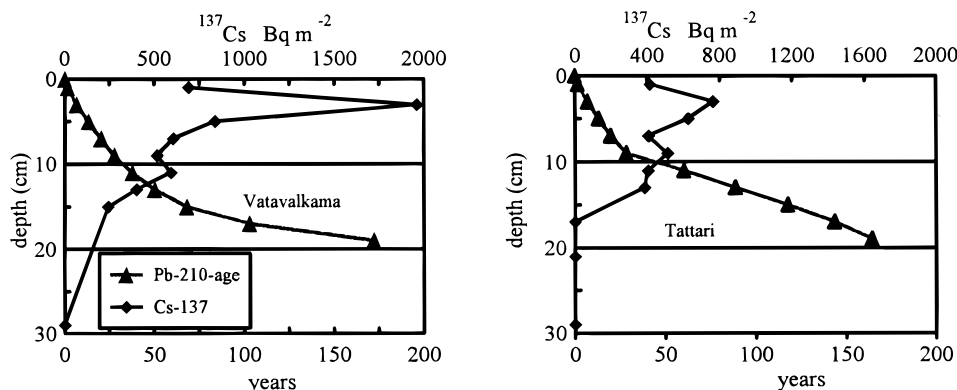


FIGURE 2.  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  based dating of sediment profiles at Vataavalkama and Tattari in the pulp mill recipient of Southern Lake Saimaa.  $^{137}\text{Cs}$  peaks ( $-3$  and  $-9$  cm to  $-11$  cm) indicate Chernobyl fallout (1986) and the smaller shoulder at the greater depth the fallout in 1963–1964 from nuclear bomb explosions in the atmosphere.

## Material and Methods

**Description of the Study Area.** The Saimaa Lake system is largest body of freshwater in Finland, 1150 km<sup>2</sup> (Figure 1), with a catchment area of 61 000 km<sup>2</sup>. The oligotrophic Lake Saimaa drains through River Vuoksi (mean discharge 600 m<sup>3</sup> s<sup>-1</sup>) into Lake Ladoga (in Russia) and with a much lower volume through the Saimaa Canal (mean 2 m<sup>3</sup> s<sup>-1</sup>) into the Gulf of Finland. The sediment sampling sites selected for this study, Vataavalkama and Tattari are located at the southeast corner of Lake Saimaa (61°15'N, 28°49'E, Figure 1). The first small pulp and paper mill was started in 1895, 35 km upstream of Vataavalkama. A large (1000 t of pulp day<sup>-1</sup>) pulp and paper mill was started in 1948 on the shore of Lake Saimaa, 3 km from the sampling site Vataavalkama and 5 km partly upstream from the site Tattari. A second smaller pulp mill (300 t day<sup>-1</sup>) near the large one started discharging in the 1970s. Chlorine bleaching of pulp in the mills started in 1954.

Pyylampi and Mustalampi are forest lakes located at ca. 20 km from the mills (61°23'N, 28°24'E) with surface areas of 0.063 and 0.0068 km<sup>2</sup> and catchment areas 3.2 and 0.5 km<sup>2</sup>, respectively. The history of forest management in the catchment area is described elsewhere (11). Sediments were harvested and dated by in the depth gradients of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  as described elsewhere (11).

**Experimental Methods.** Organic halogen was extracted with tetrahydrofuran from acidified lyophilized sediment and analyzed using a Euroglas halogen analyzer (Delft, The Netherlands) as described elsewhere (11). The adsorbable organic halogen (AOX) was analyzed according to ISO Standard 9562 (12). The carbon content in the freeze-dried sediments was analyzed with LECO CHN-analyzer (Leco Corporation, St. Joseph, MI).

For the analysis of inorganic elements 32% nitric acid (Instra-analyzed reagent for trace metal analysis; J. T. Baker, Phillipsburg) and 30% H<sub>2</sub>O<sub>2</sub> (Merck, Darmstadt, Germany) were added in a ratio 3:1 (v/v) to the weighted freeze-dried sediments. Samples were microwave digested (Milestone, mls 1200 M) with the sequence 250 W, 1 min; 0 W, 2 min; 250 W, 5 min; 400 W, 5 min; and 600 W, 5 min. Microwave-digested samples were diluted in demineralized water and analyzed with ICP-mass spectroscopy (Fisons Plasma Quard PQ 2+ VG Elemental Winsfont, U.K.) using indium as an internal standard.

## Results

Figure 2 displays the results of  $^{210}\text{Pb}$  dating of sediments from Vataavalkama (3 km) and Tattari (5 km from discharge point). The peak of  $^{137}\text{Cs}$  shows the location of the year 1986 (Chernobyl fallout) at Vataavalkama ( $-3$  cm) and Tattari ( $-3$

cm). The shapes of  $^{137}\text{Cs}$  curves indicate that there was no significant vertical mixing. The shoulders of the  $^{137}\text{Cs}$  peak at the depths of 9 cm at Vataavalkama and 11 cm at Tattari very likely are from the fallout in 1963–1964 of nuclear bomb experiments in the atmosphere. The locations of  $^{137}\text{Cs}$  peaks thus confirmed the  $^{210}\text{Pb}$  dating results. The sediments of the forest lakes Pyylampi and Mustalampi were similarly dated and showed no sign of vertical mixing (results described elsewhere; 11).

Figure 3 displays the rates of apparent sedimentation of dry matter, organic halogens, and carbon retrospectively calculated over 100 years for the Lake Saimaa sites and the two nonrecipient forest lakes. Figure 4 displays the accumulation of trace elements at the same sites.

**The Preindustrial Era (mid-1800 to 1940s).** The sedimentation of dry matter (dm) in Lake Saimaa was 40–60 g dm m<sup>-2</sup> year<sup>-1</sup> at Vataavalkama and 60–150 g at Tattari in the period from 1880 to about 1940 (Figure 3). This is equal to or lower than that in the nonrecipient forest lakes (120–200 g dm m<sup>-2</sup> year<sup>-1</sup> Pyylampi and 28–48 g dm m<sup>-2</sup> year<sup>-1</sup> Mustalampi). Before 1900, the accumulation of organically bound halogen (EOX) (Figure 3) was much lower in the Lake Saimaa (<1 mg of Cl m<sup>-2</sup> year<sup>-1</sup>) than in the nonrecipient forest Lakes Pyylampi (23 mg of Cl m<sup>-2</sup> year<sup>-1</sup>) and Mustalampi (5 mg of Cl m<sup>-2</sup> year<sup>-1</sup>). Inorganic elements accumulated similarly in the recipient and in the nonrecipient lake sediments. Mn and Zn accumulated between 5 and 40 mg m<sup>-2</sup> year<sup>-1</sup>, Cr, Cu, Ni, Pb, Sn, V between 1 and 5 mg m<sup>-2</sup> year<sup>-1</sup>, and As, Cd, Co, Hg accumulated less than 1 mg m<sup>-2</sup> year<sup>-1</sup>. Sediment accumulation of Pb increased 2-fold in all study areas, recipient and nonrecipient, between 1900 and 1940s (Figure 4).

**The Industrial Era (Mid-1940s to 1980s).** After the arrival of a large pulp mill in the Lake Saimaa area in 1948, the sedimentation rate increased 6-fold, reaching 290 g dm m<sup>-2</sup> year<sup>-1</sup> at Vataavalkama and 210 g dm m<sup>-2</sup> year<sup>-1</sup> at Tattari by the end of 1980s. The sediment accumulation rate of EOX in the pulp mill recipient area increased from the 1950s to the 1980s to 1350 mg of Cl m<sup>-2</sup> year<sup>-1</sup> at Vataavalkama and to 500 mg of Cl m<sup>-2</sup> year<sup>-1</sup> at Tattari (Figure 3). This is 1000–10000 times higher than was found at these sites of Lake Saimaa before the year 1900 (not visible in Figure 3). The concentrations of EOX–Cl were 4900 and 2900 mg of EOX–Cl g<sup>-1</sup> dw in the most polluted layers of Vataavalkama and Tattari, respectively. The increase of EOX accumulation paralleled the increase in the use of chlorine for the bleaching of pulp in the discharging mills (Figure 5). In the nonrecipient forest Lakes Mustalampi and Pyylampi, the accumulation rates of EOX increased in the same period only from 5–10 mg of Cl m<sup>-2</sup> year<sup>-1</sup>. The accumulation of sediment carbon increased from 11 g of C of m<sup>-2</sup> year<sup>-1</sup> in the 1940s to 57 g

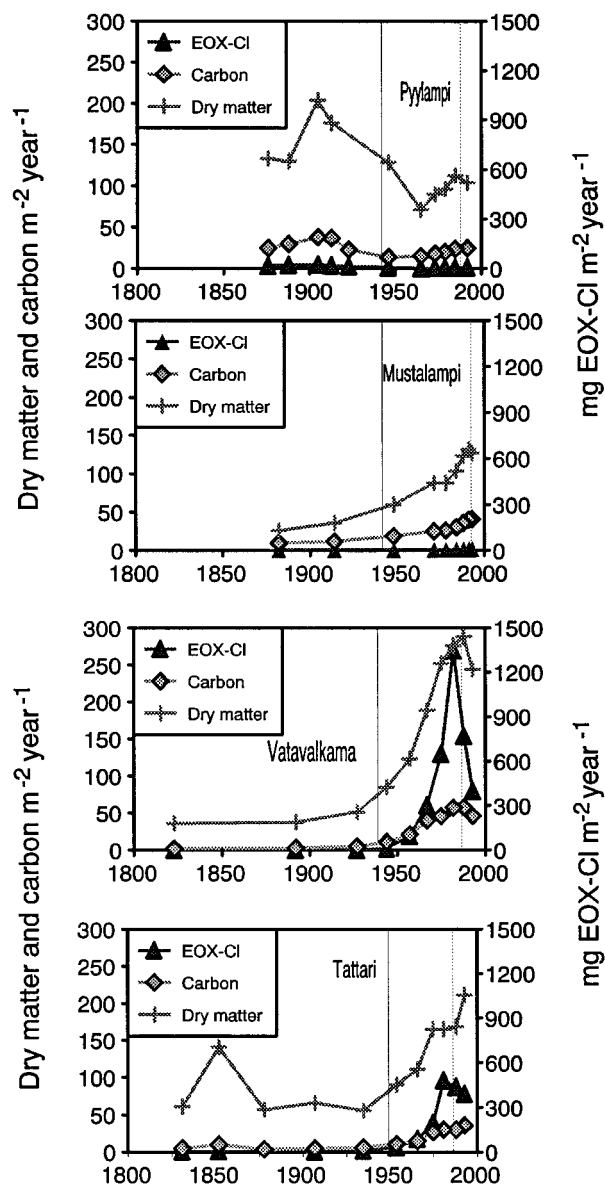


FIGURE 3. Sediment deposition rates of carbon, dry matter, and tetrahydrofuran soluble organic halogen (EOX-Cl) in the pulp mill recipient area of Southern Lake Saimaa and in two nonrecipient forest lakes. The peak sedimentation around 1850 at Tattari may connect to the sedimentation of eroded soils as the result of Lake Hyytiäinen (6–7 m) eruption into Lake Saimaa. The vertical lines indicate the start of industrial (—) and the environmental investments era (···).

of  $C\ m^{-2}\ year^{-1}$  in 1980s at Vataavalkama and from 5.4–30  $g\ C\ m^{-2}\ year^{-1}$  at Tattari, but were thereafter no higher than those in the nonrecipient lakes Mustalampi ( $52\ g\ m^{-2}\ year^{-1}$ ) and Pyylampi ( $30\ g\ m^{-2}\ year^{-1}$ ).

After the 1940s, the accumulation rates of trace elements increased at both the polluted and the nonrecipient sites. The accumulation increase of Pb was similar at all sites from 4–5 to 6–14  $mg\ m^{-2}\ year^{-1}$  and may be due to air pollution. The accumulation rates of As, Cd, Cr, Cu, Hg, Mn, Ni, Sn, Zn and V increased in the recipient area as well as in the Lake Mustalampi since 1940s by 2–5-fold, reaching levels of 1–5  $mg\ m^{-2}\ year^{-1}$  (As and Sn), 5–40  $mg\ m^{-2}\ year^{-1}$  (Cr, Ni, Cu, and V), >40  $mg\ m^{-2}\ year^{-1}$  (Mn and Zn), and <1  $mg\ m^{-2}\ year^{-1}$  (Cd and Hg). In Lake Mustalampi, the accumulation rates of heavy metals (other than Hg and Pb) were higher than in Lake Pyylampi. The accumulation rates of most elements in Lake Saimaa at Vataavalkama and Tattari thus

were similar to those in Lake Mustalampi. One source for accumulation of heavy metals after the entry of large-scale forest industry in the area may be the runoff from forest harvesting, storage, timber floating, and debarking of logs. In the area of the forest lakes, the canopy was harvested and wetland drained around the 1960s, and harvested forest ground around Mustalampi was burned (1965) and new canopy planted (1965).

**The Era of Environmental Protection Investments (1987–present).** From 1987–1991, elemental chlorine in the mill bleach plants was stepwise completely substituted by chlorine dioxide. An advanced activated sludge plant operated full scale since 1993. Mid-1980s timber floating was discontinued, and the local industry (pulp, steel) went over from oil and coal to natural gas as the fuel. The sediment accumulation rate of EOX decreased after 1990 by 70% to 400  $mg\ of\ Cl\ m^{-2}\ year^{-1}$  at Vataavalkama and to 390  $mg\ of\ Cl\ m^{-2}\ year^{-1}$  at Tattari (Figure 3). Even so, this is 40–50 times higher than EOX accumulation in nonrecipient lakes Mustalampi and Pyylampi in the same period. The decrease in EOX accumulation coincided with the replacement of elemental chlorine by chlorine dioxide. The previously increasing trend of the rates of the sedimentation and the accumulation of sediment carbon changed to decreasing trends, 240  $g\ dm\ m^{-2}\ year^{-1}$  and 46  $g\ of\ C\ m^{-2}\ year^{-1}$  at Vataavalkama and 210  $g\ dm\ m^{-2}$  and 36  $g\ of\ C\ m^{-2}\ year^{-1}$  at Tattari.

In the 1980s, the sediment accumulation of Ni, V, and As leveled off in the pulp mill recipient area. In the pulp mill recipient area and in the nonrecipient lakes, the accumulation rates of Cd and Hg remained <1  $mg\ m^{-2}\ year^{-1}$ . The accumulation rates of Pb only slightly decreased despite the complete transition to unleaded fuel in cars in Finland after 1980s. The accumulation of Zn, Mn, and Cu no longer increased in the pulp mill recipient area or in Lake Mustalampi, possibly relating to the discontinuation of timber floating (Lake Saimaa) and cessation of harvesting of the canopy in the area (Lake Mustalampi).

**Recalcitrance of Sediment Contained EOX.** Figure 5 displays the consumption of chlorine chemicals from 1955–1995 and the discharges of organic halogen from mills, expressed as AOX. The cumulative discharge from 1955–1996 was 48 400 t of AOX-Cl. The peak discharge, 2500 t of AOX  $year^{-1}$  (1980–1985, Figure 5), coincided with the accumulation maximum of EOX in the sediment in 1980s (Figure 3).

To assess the persistence of organic halogens in the sediments, the sediment accumulation of EOX was calculated per ton of AOX discharged (Figure 6). The result shows that, at Vataavalkama (3 km), 0.3–0.6  $mg\ of\ EOX-Cl\ accumulated/m^2\ of\ the\ sediment\ from\ each\ ton\ of\ AOX-Cl\ discharged\ by\ the\ mill\ and\ at\ Tattari\ (5\ km)\ 0.1-0.6\ mg\ of\ EOX-Cl\ m^{-2}$ . There was only a slight downward trend in the accumulation increment of EOX from the younger (1980s) toward older (1950s) sediment layers. When an exponential curve is fitted to the data, a half-life of 60–80 years for organic halogen of pulp mill origin can be estimated (Figure 6).

In Figure 6, the oldest EOX accumulation increment for Vataavalkama is likely too low [0.3  $mg\ of\ EOX-Cl\ m^{-2}\ (ton\ AOX-Cl\ discharged)^{-1}$ ] because the bleaching started in 1954, and this layer may contain deposits formed before the onset of pulp bleaching. In the most recent sediment layers at Tattari and Vataavalkama, the accumulation increment of EOX was 0.6  $mg\ of\ Cl\ m^{-2}\ (ton\ AOX-Cl\ discharged)^{-1}$ , much higher than for the older layers. This may partly result from changes of water flow by the constructed dams (Figure 1). It may also indicate that the AOX discharged in biologically purified wastewater (1993) had a greater tendency of sediment accumulation and of spreading over a larger distance (Tattari)

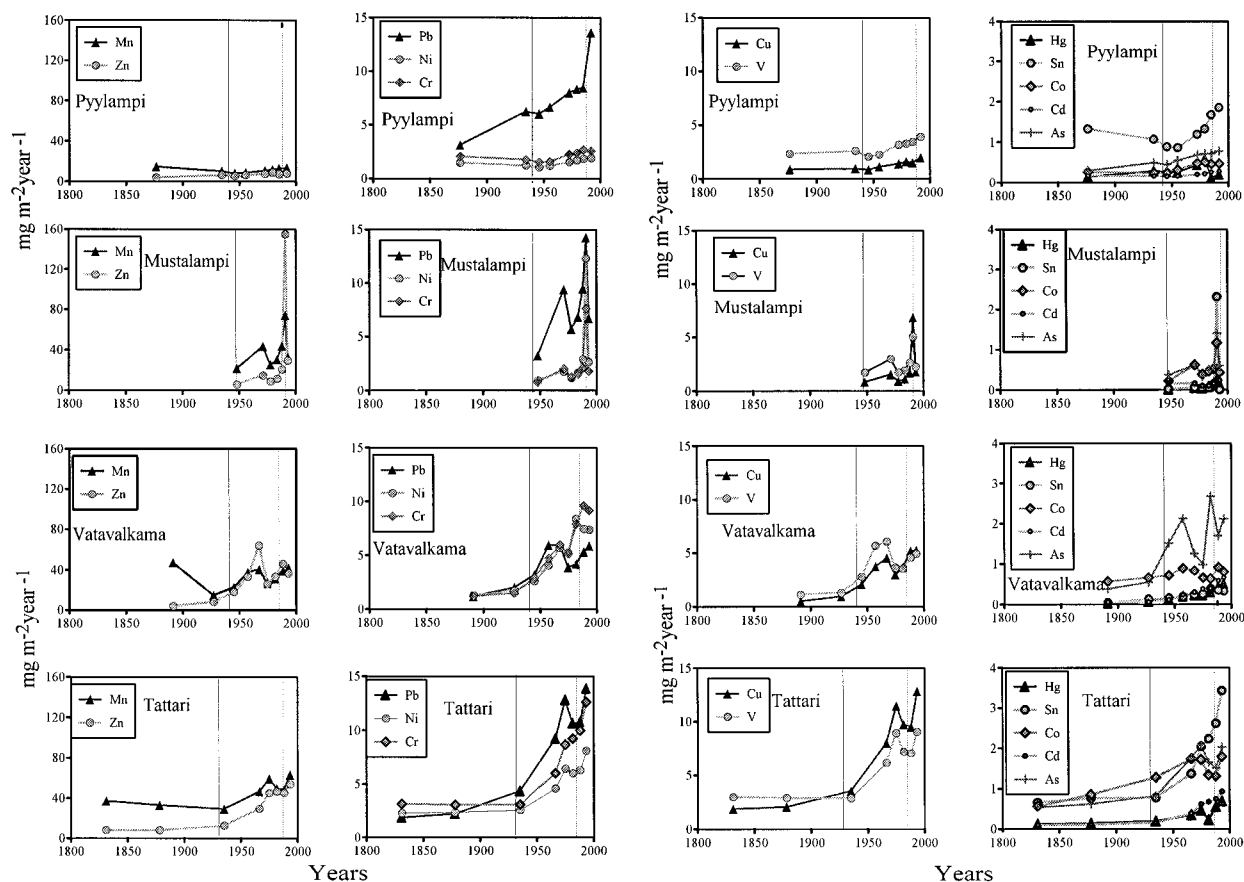


FIGURE 4. Sedimentation rates of heavy metals in the recipient area of pulp mills in the southeastern Lake Saimaa and in two nonrecipient lakes, Pyylampi and Mustalampi, of the same geographical area. The vertical lines as explained in Figure 3.

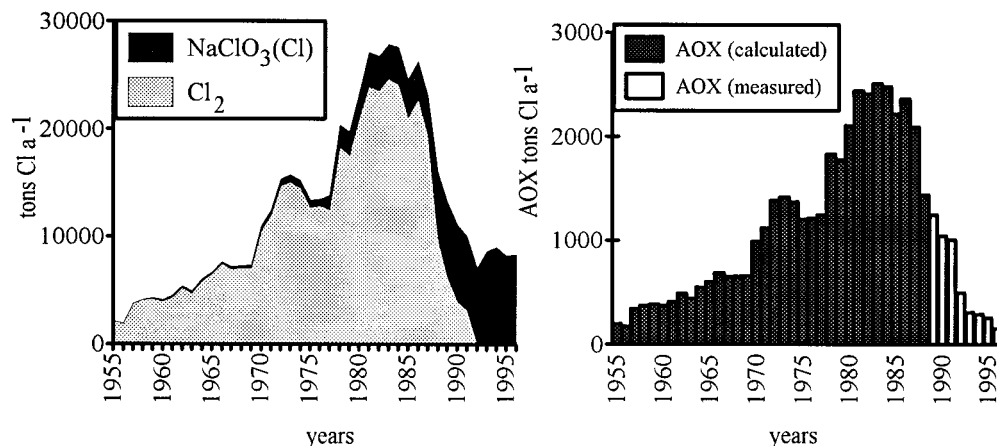


FIGURE 5. Chlorine chemicals usage and AOX discharges by pulp mills in the study area of southeastern Lake Saimaa. (Left panel) Chlorine chemicals usage. (Right panel) Discharge of AOX-Cl into the recipient. The discharges until 1989 were calculated on the basis of analysis showing that 9% of chlorine when  $\text{Cl}_2$  was used, became converted to organic form, adsorbable to active carbon (=AOX). From 1989 onward the data represent measured discharges.

from the factory than did the previously discharged AOX that had not undergone biological treatment.

## Discussion

This paper describes the rates of sediment accumulation of organic halogen, carbon, and selected trace elements over a period of 100 years, during which the southern Lake Saimaa area changed from an oligotrophic, pristine area to a moderately inhabited area with intensive pulping industry. Furthermore, it is an attempt to evaluate the pollution legacy hidden in lake sediments from the early decades of pulping industry and the impact of improvements achieved by huge environmental investments by the industry mid-1980s.

Table 1 compares the accumulation rates of Cd, Cu, Hg, Ni, Pb, V, and Zn observed in this study with those of other studies in Finland and in northern Sweden before and after industrialization. Our data from preindustrial era (<1940) showed accumulation rates of Cd, Cu, Hg, Ni, Pb, V, and Zn in Lake Saimaa, Lake Mustalampi and Lake Pyylampi similar to those reported elsewhere for forest lakes in SE Finland and northern Sweden (13, 14). Sources for increased accumulation of these heavy metals in Lake Saimaa and Mustalampi areas after 1940s may be forest management such as harvesting, storing, forest floor burning for the forest lake and timber floating and debarking of logs for the Saimaa

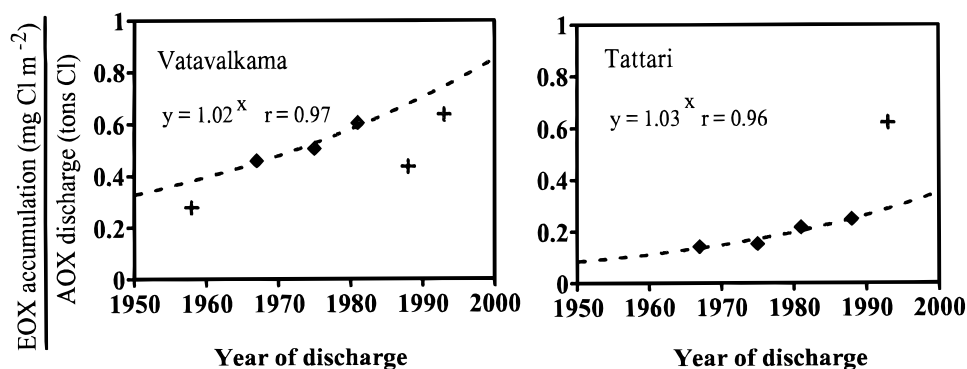


FIGURE 6. Sediment accumulation tendency of organic halogens discharged from bleached kraft pulp mills. The sediment accumulation of EOX was measured at 3 km (Vataavalkama) and at 5 km (Tattari) from the discharge point and plotted against the known and calculated discharges (Figure 5) of AOX.

TABLE 1. The Accumulation Rates of Heavy Metals in the Recent 100 Years in Finnish and Swedish Lakes; Combined from the Data Presented in this Paper and Refs 13 and 14

	no. of lakes	(mg m <sup>-2</sup> year <sup>-1</sup> )							source of data
		Cd	Cu	Hg	Ni	Pb	V	Zn	
lakes Pyylampi, Mustalampi, and Saimaa									
1880–1940	3	0.1–0.2	0.8–3.5	0.1–0.3	0.9–2.6	3.0–4.6	0.5–2.9	4.1–12.6	this study
1950–1985	3	0.1–0.7	0.8–11.5	0.1–0.6	0.9–12.3	3.1–14.3	1.7–8.9	5.5–64.3	this study
1985–1995	3	0.3–0.9	1.5–12.8	0.2–0.7	1.9–8.1	5.3–13.9	2.3–9.1	7.8–53.7	this study
lakes in S-E Finland									
1940 and before	3		1.2		0.8–1.2	2–3		2–4	13
1950–1985	3		1–3	0.02–0.4	1.8–2.5	6–10	1.1–2.7	6–10	13
lakes in N Sweden									
1950–1985	7	0.15–0.30		0.01–0.1		5–15			14

area. Finnish wood ash (mainly the bark) contains 0–20000 mg of Mn, 40–6000 mg of Zn, 20–180 mg of Cu, 0–290 mg of Cr, 15–100 mg of Ni, 0.1–30 mg of Cd, and 2–60 mg of As kg<sup>-1</sup> ash of wood (E. Elomaa, Enso Oy, unpublished results). Zn was the only element for which the accumulation may directly relate to the pulping industry. It increased in the recipient area and in Lake Mustalampi. Lake Mustalampi received, in 1979, 30 m<sup>3</sup> of biologically purified kraft pulp bleaching wastewater (11).

In the pulp mill recipient area, the accumulation of V, Ni, and As decreased after the 1980s, reflecting the transition from oil and coal to natural gas by the local industry. Fossil fuels are known to contain V, Ni, and As (15–17). In the recent decades, up to 30% of the sediment accumulation observed for Zn, Cu, Mn, V, and Ni in Lakes Pyylampi and Mustalampi and in the pulp mill recipient area at Vataavalkama and Tattari could be explained by wet and dry deposition, based on the measurements at Haapasaari meteorological station (18), about 100 km south from southern Lake Saimaa. The sediment accumulation of Pb after 1900 observed by us for all sites was similar to that earlier reported for lakes in Finland (13) and Sweden (14). It is probably due to the use of Pb as gasoline additive (19).

The mills studied in the present paper used phenylmercury slimicides (about 800 kg of Hg year<sup>-1</sup>) until 1967, when these were banned (20). Yet the sediment accumulation of Hg only increased from 0.1–0.3 mg m<sup>-2</sup> year<sup>-1</sup> between the 1940s and the late 1960s at Vataavalkama 3 km from the pulp mill. This is similar to the contemporary increase of Hg accumulation in the nonrecipient forest lake sediments, but higher than that in the preindustrial era in Vataavalkama and Tattari areas (0.1 mg m<sup>-2</sup> year<sup>-1</sup>). After the discontinuation of slimicide use, no decrease of Hg accumulation was observed, indicating that sediments were not the main

environmental sink of organomercurial slimicides. The concentrations of Hg in sediments (1.1–2.1 mg of Hg kg<sup>-1</sup> dw) downstream of this pulp mill were similar to those reported for a discharge area elsewhere (0.9–1.9 mg of Hg kg<sup>-1</sup> dw; 21).

Sediments collected at Vataavalkama (3 km from pulp mill) in 1979, showed accumulation of 1700 mg of total (nitric acid digestable) organic Cl m<sup>-2</sup> year<sup>-1</sup> (calculated from the data presented in refs 6 and 7). This value is similar to that reconstructed in the present study (sampled in 1995) for the layers formed around the year 1979, 1350 mg of EOX–Cl m<sup>-2</sup> year<sup>-1</sup>. The different method analysis of analysis may account for the deficit of 20% since tetrahydrofuran extractable EOX represents only a part of the nitric digestable “total organic halogen” (22). These observations are in line with the long half-life (60–80 years) of sediment-contained organic halogens, estimated from Figure 6 in this paper. Thus, intrinsic bioremediation in the sediment may occur but it is slow. EOX from pulp mill recipient sediments has been shown to accumulate into benthic organisms (23), which may cause toxic effects on wood web.

Intensive environmental investments were made by the mills after 1985. Elemental chlorine was replaced by chlorine dioxide, which is known to induce less formation of chlorine compounds than elemental chlorine (24–26), and activated sludge treatment was installed for wastewaters, removing 40–60% of pulp mill AOX and TOC (27). Our data showed a dramatic decrease in EOX accumulation in the recipient water after these investments (Figure 3). Palm and Lammi (9) analyzed sediments in the recipient area 1 km from a pulp mill in the Pietarsaari area on the coast of the Gulf of Bothnia of the Baltic Sea. The peak accumulation of EOX in the mid 1980s was at 1 km from discharge point 1100 mg m<sup>-2</sup> year<sup>-1</sup> and decreased to 180 mg m<sup>-2</sup> year<sup>-1</sup>, after the mill changed to chlorine dioxide and installed in 1986 the

wastewater treatment plant based on activated sludge process. Using extrapolation similar to that in Figure 6, we calculated from the data in refs 9, 28, and 29 that 0.52 (1990) and 0.27 (1991) mg of EOX-Cl had accumulated  $\text{m}^{-2}$  in that sediment, (ton of AOX discharged) $^{-1}$ , and 0.19–0.16 mg of EOX-Cl  $\text{m}^{-2}$  at 1 and 11 km, respectively, from the discharge point. These figures are remarkably similar to the results reported in this paper for sediment accumulation in Lake Saimaa (Figure 6). The similarity of EOX accumulation increments, independently obtained for different recipient waters (Baltic Sea and Lake Saimaa), may indicate that accumulation increment of pulp mill discharged AOX may be similar in different mills and different recipients.

## Acknowledgments

Financial support was provided by the Academy of Finland, Maj ja Tor Nessling Foundation, and Helsinki University Center of Excellence Fund. We are grateful to Timo Jaakkola (University of Helsinki, Laboratory of Radiochemistry), Håkan Wikberg (Kemira Chemicals), Eila Elomaa, Hilka Hännikäinen, and Henry Lindell (Enso company), and Pekka Lehonkoski (Forest Information Center) for their contributions and for collecting data.

## Literature Cited

- (1) Asplund, G.; Grimvall, A. *Environ. Sci. Technol.* **1991**, *24*, 1346.
- (2) Fernandez, M. A.; Hernandez, L. M.; Gonzales, M. J.; Tabera, M. C. *Water, Air Soil Pollut.* **1992**, *65*, 293.
- (3) Harper, D. B. *Nature* **1985**, *315*, 55.
- (4) Lovelock, J. E. *Nature* **1975**, *256*, 193.
- (5) Kankaanpää, H. T.; Lauren, M. A.; Saares, R. J.; Heitto, L. V.; Suursaar, U. K. *Environ. Sci. Technol.* **1997**, *31*, 96.
- (6) Salkinoja-Salonen, M.; Saxelin, M.-L.; Pere, J.; Jaakkola, T.; Saarikoski, J.; Hakulinen, R.; Koistinen, O. In *Advances in the Identification & Analysis of Organic Pollutants in Water*; Keith, L. H., Ed.; Ann Arbor Science Publishers Inc. Ann Arbor 1981; Vol. 2, pp 1131–1164.
- (7) Salkinoja-Salonen, M. S.; Valo, R.; Apajalahti, J.; Hakulinen, R.; Silakoski, L.; Jaakkola, T. In *Current Perspectives in Microbial Ecology*; Klug, M. J.; Reddy, C. A., Eds., American Society for Microbiology, Washington DC, 1984; pp 668–676.
- (8) Johansson, P.; Rappe, C.; Kjeller, L.-O.; Kierkegaard, A.; Håkanson, L.; Johnson, B. *Ambio* **1993**, *22*, 37.
- (9) Palm, H.; Lammi, R. *Environ. Sci. Technol.* **1995**, *29*, 1722.
- (10) Sasaki, E. K.; Salonen, K.; Vähätalo, A.; Salkinoja-Salonen, M. S. In *The Contaminants in the Nordic Ecosystem: Dynamics, Processes & Fate*; Munawar, M.; Luotola, M., Eds., SPB Academic Publishing: Amsterdam, 1995; pp 109–123.
- (11) Suominen, K. P.; Jaakkola, T.; Elomaa, E.; Hakulinen, R.; Salkinoja-Salonen, M. S. *Environ. Sci. Pollut. Res.* **1997**, *4* (1), 21.
- (12) International Standardization Organization. International Standard ISO 9562. Water Quality—Determination of Adsorbable Organic Halogens; Geneva, 1989.
- (13) Verta, M.; Tolonen, K.; Simola H. *Sci. Total Environ.* **1989**, *87/88*, 1.
- (14) Renberg, I. *Hydrobiologia* **1986**, *143*, 379.
- (15) Docekal, B.; Krivan, V.; Pelz, N. *Fresenius J. Anal. Chem.* **1992**, *343*, 873.
- (16) Ganor, E.; Alshuller, S.; Foner, H. A.; Brenner, S.; Gabby, J. *Water, Air Soil. Pollut.* **1988**, *42*, 241.
- (17) Youngs, W. D.; Rutzke, M.; Guttermann, W. H.; Lisk, D. J. *Chemosphere* **1993**, *27*, 1269.
- (18) Leinonen, L. (Ed.) *Air Quality measurements*; Finnish Meteorological Institute, Helsinki, **1995**; pp A97.
- (19) Hurst, R. W.; Davis, T. E.; Chinn, B. D.; *Environ. Sci. Technol.* **1996**, *30*, 304.
- (20) Häsänen, E. *Ympäristö ja Terveys* (in Finnish) **1975**, *6*, 515.
- (21) Meinelt, T.; Gruger, R.; Pietrock, M.; Osten, R.; Steinberg, C. *Environ. Sci. Pollut. Res.* **1997**, *4* (1), 32.
- (22) Sasaki, E. K.; Salonen, K.; Vähätalo, A.; Salkinoja-Salonen, M. S. In *Environmental fate and effects of pulp and paper mill effluents*; Servos, M. R.; Munkittrick, K. R.; Carey, J. H.; Van der Kraak, G. J., Eds.; St. Lucie Press Delray Beach, FL, 1996; pp 261–270.
- (23) Sasaki, E. K.; Mikkola, R.; Kukkonen, J. V. K.; Salkinoja-Salonen, M. S. *Environ. Sci. Pollut. Res.* **1997**, *4* (4), 194.
- (24) Axegård, P. *Pulp Paper Can.* **1989**, *90*, 78.
- (25) Stichfied, A. E.; Woods, M. G. *Tappi J.* **1995**, *78*, 117.
- (26) Wilson, R.; Swaney, D. C.; Luthe, C. E.; O'Connor, B. I. *Pulp Paper* **1995**, *95*, 35.
- (27) Jokela, J. K.; Laine, M.; Ek, M.; Salkinoja-Salonen, M. *Environ. Sci. Technol.* **1993**, *27* (3), 547.
- (28) Karessuo, A., Ed. *Environmental yearbook 1991*; Finnish Association of Forest Industries, Helsinki, 1991.
- (29) Karessuo, A., Ed. *Environmental yearbook 1992*; Finnish Association of Forest Industries, Helsinki, 1992.

Received for review October 9, 1997. Revised manuscript received March 16, 1998. Accepted March 18, 1998.

ES9708880