Organic Halogens in the Environment: Studies of Environmental Biodegradability and Human Exposure

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Organic halogens from chlorobleaching of kraft pulp were not as biorecalcitrant as has been assumed. Fifty percent were removed during biotreatment of wastewater, and 50% of the remaining organohalogens faded in fresh water ecosystems in 200 to 400 days. Molecular size seemed not to hinder biodegradation up to sizes of approximately 2000 daltons. Anoxic biodegradation was of prime importance for halomineralization of pulp bleaching organohalogens but could also lead to toxic metabolites such as vinyl chloride from tri- and tetrachloroethene in anoxic soil. Indigenous soil microbes were unable to clean old organohalogen pollution but had converted chlorophenols into polymeric substances, chlorohumus, which were found bioaccumulable by earthworms in spite of the large (up to 5000 g/mole) molecular sizes. Because of the danger of formation of toxic metabolites, the biochemistry of the xenobiotic degradation must be elucidated before active bioremediation is practiced on polluted soil or water. Groundwater pollution by chlorophenols led to increased disease among the exposed population in one well-studied case. Two further cases of potential environmental health impact are described. — Environ Health Perspect 103(Suppl 5):63–69 (1996)

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Introduction

Environmental Contamination by Organic Halogens

A major part of pesticides and other hazardous organic chemicals in the environment are halogen compounds. This group of chemicals is responsible for most cases of groundwater contamination (1). About 12,000 metric tons Cl in organic halogens was discharged into the environment in Finland in 1992. Approximately half of this (4900 tons in 1992) came from bleaching of paper pulp and was discharged into the waterways. In 1992, the specific load of one ton of pulp was 1 kg of organic halogen, expressed as AOX.

Chlorophenols have long been used as antibluestain and antisapstain agents in timber and lumber in most industrialized countries. Until 1984, the use of chlorophenols for wood preserving (about 1000 tons of organic halogen per year) was the second largest discharge of organic halogens into the environment in Finland. Chlorophenol use ceased in Finland in 1984, but the pollution of soil, subsurface, and groundwater persists, potentially leading to human exposure. The third important organic halogen discharge came from the use of halogenated solvents, tetrachloroethene, trichloroethene, 1,1,1-trichloroethane, and methylene chloride, totaling approximately 2000 tons per year. One PVC mill discharges about 2000 tons per year of vinyl chloride per year (2). The wet deposition of organic halogens in Finland has been estimated as 1600 tons per year (3) and reflects incineration discharges, since organic halogens are synthesized from organic matter by fire. The carbon-halogen bond is thought to be biologically recalcitrant; this is evidenced by the accumulation of organic halogens such as PCBs and haloorganic pesticides in the food chain.

Biodegradation and Human Exposure to Chlorobleaching Organic Halogens in the Environment

Biodegradation during Wastewater Biotreatment

The large chlorine-containing molecules originating from the reaction of chlorine chemicals with lignin (pulp bleaching) and from the reaction of chlorophenols with soil humus are often assumed to be biologically inert (not permeating into live cells and hence poorly biodegradable).

We investigated the bioremoval of the organic carbon and organic halogen in bleached kraft pulp mill wastewater during the purification of the wastewater and later on in the recipient lake ecosystem. Table 1 shows examples of the removal of dissolved organic carbon (DOC, ISO standard 8245) and halogen (active carbon-adsorbable organic halogen, AOX, ISO standard 9562) by an activated sludge (Mill A) and an anaerobic-aerobic lagoon system (Mill C).

Results in Table 1 and similar findings reported elsewhere (4), show that the percentage of AOX removal during biopurification of wastewater was around 50%. The removal efficiency was similar, about 50%, for both the carbon and the halogen. Thus, the ratio of carbon to halogen in the wastewater-dissolved organic matter was the same before and after biotreatment, 10 to 15:1 (C:Cl, by weight) or 35 to 45:1 (by mole).

Evaporation and adsorption of AOX to biosludge have been shown to explain less than 5% of the organic halogen bioremoval (5,6); therefore, the major portion of bioremoval seems to be true mineralization. The table also shows that anaerobic
Table 1. Bioremoval of organic carbon.

| Mill | Month | mg C/l influent | % removed | DOC | mg C/l influent | % removed | AOX | mg C/l influent | % removed |
|------|-------|-----------------|-----------|-----|-----------------|-----------|-----|-----------------|-----------|
| A    | April | 833             | 12        | 58  | 100             | 23        | 52  |
| A    | May   | 762             | 4         | 52  | 58              | 26        | 55  |
| A    | Sept  | 750             | 2         | 42  | 73              | 11        | 49  |
| C    | April | 541             | 13        | 52  | 52              | 50        | 63  |
| C    | May   | 637             | 34        | 56  | 61              | 57        | 66  |
| C    | Oct   | 509             | 15        | 46  | 49              | 42        | 58  |
| C    | Dec   | 480             | 14        | 52  | 34              | 53        | 65  |

Bioremoval of dissolved organic carbon (DOC, ISO 8245) and active carbon adsorbable organic halogen (AOX, ISO 9962) from bleached kraft pulp mill wastewater by activated sludge and anaerobic/aerobic lagoon treatment. Mill A (50,000 m³ wastewater per day) had an equalizing basin (25,000 m³) followed by an activated sludge treatment (25,000 m³ gross volume) plant. Mill C had an equalizer, an anaerobic lagoon, and an anaerobic lagoon with hydraulic retention times of 1.2, 3, and 6.4 days, respectively.

Figure 1 illustrates the molecular weight distribution of wastewater from a bleached kraft pulp mill before (solid lines) and after (broken lines) biological purification. Wastewater treatment was by activated sludge (AS) or an anaerobic-aerobic lagoon system (AL). A) UV-Vis absorbing compounds; B) organic halogen compounds. The size exclusion chromatograms shown were obtained with Ultrastyragel 10000A + 1000A + 500A + 100A styrene divinyl benzene copolymer columns connected in series and eluted with tetrahydrofuran.

Lagooning was surprisingly efficient in removing organic halogen from the wastewater while it did little to remove DOC.

Figure 1 summarizes the molecular size distribution changes of the organic halogens during the biotreatment of wastewater in the two treatment plants during warm and cold seasons in 1991. The size distributions were determined by high performance size exclusion chromatography (HP-SEC) using both synthetic lignin oligomers (and commercially available monoaromatic substances and monodisperse polystyrenes for calibration) (7,8). The figure shows the molecular size distribution of organically bound halogens in the wastewater before and after biotreatment. The analytical method is described in detail elsewhere (9).

It is seen from Figure 1 that both the activated sludge and the lagoon system removed all size classes of organic halogen compounds with similar efficiency. It also shows that the overall size of the organic halogens in bleached kraft pulp mill wastewater was not high: almost all of the organically bound halogen appeared in chromatographic fractions of < 2000 g/mole.

Biodegradation in a Freshwater Ecosystem

We investigated the biodegradation behavior of the purified bleached kraft pulp mill wastewater (Mills A and C of Table 1 and Figure 1) in large outdoor mesocosms. The biologically purified wastewater was diluted (2–11% by vol) into natural lake water in 17 enclosures (polyethylene), each holding 2 m³ and placed floating in the lake. Reference enclosures were filled with lake water only. The mesocosms had a closed bottom, allowing for the calculation of mass balance for the enclosed organic halogens. The wastewaters were blended and incubated in two different lakes, one humic and the other with clear water. Both lakes were pristine, and the lake waters contained little AOX (< 0.05 mg/l) before the wastewater was introduced. To distinguish biodegradation from photocatalysis, a number of replicate mesocosm enclosures were covered with black plastic and incubated in the dark under otherwise identical conditions.

One series of mesocosms was started in June and another series was started in November. Details of this experiment are described elsewhere (10,11), but Figure 2 summarizes the kinetics of AOX removal during the first 300 days. Figure 2 shows that the initial disappearance of AOX (starting from 0.6–3 mg/l of AOX, depending on wastewater dilution) was much faster when the run was started in June as compared to one started in November. AOX removal also was faster in light-exposed cosolvents than in their darkened counterparts when the run was started in June; no such difference was seen in the run started in November, probably because of the ice cover that withheld light from all enclosures during the 5 months after November.

Irrespective of the initial removal rates, the two experiments gave similar half-life patterns for AOX—about 1 year (200–400 days). We collected and analyzed the sediments formed in the enclosures during 300 days and found that, although the concentration of organically bound halogen was higher in the sediment section than in the water column, the sediment contributed only about 0.5% of the total mesocosmic organic halogen because of its small volume.

Our observed decay of AOX under conditions mimicking nature was faster than the 2-year half-life estimated by Grimvall et al. (12) in Swedish lakes. The long half-life observed by the Grimvall group is actually surprising because they studied the AOX removal from wastewater that was mechanically purified only, whereas our wastewater had already undergone biological treatment. This may indicate that halogen compounds that are biodegradable under biological wastewater treatment may not be readily biodegradable under environmental conditions.

In conclusion, our studies support the view of relative recalcitrance of at least a part of the bleached kraft pulp mill organic halogens; approximately 25% of the wastewater contained organic halogens that persisted through biological purification followed by one year of exposure to the lake ecosystem.

Exposure Studies

Shallow inland lakes in Finland are the typical recipients of industrial wastewaters from the pulp and paper industry. In some cases, there are communities downstream of mills that use the same water for drink-
ing water. Also in cases where there is no industrial point source upstream, Finnish rivers and lakes contain a high concentration of organic carbon, typically 6 to 12 mg C/l. This carbon is a source of organic halogens when chlorine disinfection is practiced.

It is known that long-term use of chlorine disinfected drinking water causes an increased risk to some serious diseases, e.g., cancers of the urinary tract (13). Studies conducted by the Finnish National Cancer Registry indicated an almost 2-fold incidence of some cancers among the half of the population served with surface water from which chlorine-disinfected drinking water was made versus the other half of the population served with ground water, which is not or is only incidentally chlorine disinfected (E. Pukkala, personal communication). The presence of haloforms and various mutagenically active small molecules has long been recognized in chlorine-disinfected tap water. These molecular species constituted less than 1% of the organic halogens present in drinking water from chlorine-disinfected surface water (3). We measured the content of organic halogens (AOX) in urine of persons consuming drinking water with varying known concentrations of AOX and found statistically significant positive correlation between AOX in urine and AOX in drinking water (Figure 3). When extrapolated to drinking water concentration of AOX = 0 µg/l, the (night) urine contained about 70 µg AOX/l (Figure 3). The high concentrations in some drinking water seemed to increase manifold the urine background concentration of AOX.

Figure 4 displays a size exclusion chromatogram of one drinking water heavily contaminated with organic halogens (320 µg AOX/l). The raw water used by the water works of this city (~ 40,000 residents) contained about 1% (by vol) of wastewater from a bleached kraft pulp mill 65 km upstream. It shows that molecular weight averages of the organic halogens 730 g/mole (M₆) and 160 g/mole (M₃), are similar to those found in the wastewater of the mill that contaminates the river, 540 g/mole (M₆) and 250 g/mole (M₃) from the same time period (designated as Mill D by Jokela and Salkinoja-Salonen) (9). Our conclusion from these studies is that such molecules were indeed resorbed by the human gut and excreted (partially?) in urine.

**Wood-preserving Chlorophenolic Compounds**

**Human Environmental Exposure**

The chlorophenol formulation used in Finland for wood preserving is a 2% solution in water, made to pH 10 to pH 11 with sodium hydroxide. It contains 2,3,4,6-tetrachlorophenol (80%), 2,4,6-trichlorophenol (7–15%), pentachlorophenol (5–10%), other chlorophenols (up to 1%), and impurities such as polychlorinated phenoxycyanals (8 congeners, totaling 9000 mg/kg), dibenzofurans, and dibenzofuran-p-dioxins (12 congeners, totaling 200 mg/kg) (15–17). Chlorophenols have been shown to spread both vertically and horizontally and have led to numerous cases of ground water pollution (15,17). The dimeric impurity components were found...
to attach firmly onto soil particles and showed little tendency to leach (16,18,19).

One case of ground water contamination by chlorophenols, which leached from saw mill property at Kärkölä in southern Finland, led to serious long-term exposure of about 2000 residents. Health effects have been extensively studied at this site. The community groundwater well was located 800 m down hill from the saw mill. The well water was found to contain 73 µg of trichlorophenol, tetrachlorophenol, and pentachlorophenol per liter in November 1987. Since the contamination persisted in December (70–140 µg chlorophenols per liter), the distribution of well water to consumers was discontinued (20). However, the creek leading from the well into a nearby lake was also contaminated, and the study of dated lake sediments from the creek delta area showed that the well must have been contaminated for a long time, possibly since 1962 when the water works were constructed (21).

Also, fish from the lake were contaminated by chlorophenols: up to 5 mg of 2,4,6-trichlorophenol, 10 mg of 2,3,4,6-tetrachlorophenol, and 1.2 mg of penta-chlorophenol were found per kg of fish fat. This increased the chlorophenol exposure of the residents that consumed the fish (20). Closer study of the groundwater aquifer found extremely high concentrations of chlorophenols (56–190 mg/l) and traces of polychlorinated dibenzodioxins and dibenzofurans, indicating a giant burst of wood-preserving liquor into the highly porous morene soil above the aquifer (22).

Chlorophenols were found in blood and urine of the exposed population in quantities higher than those from the nonexposed controls from neighboring communities. Medical studies showed and cancer registry data revealed health damage unequivocally correlated to the exposure. Non-Hodgkin’s lymphoma and soft-tissue sarcoma were found in excess in the exposed population (23). Eczema, gastrointestinal discomfort, headache, malaise, anorexia, tiredness, and respiratory infections were also increased among the affected population (24).

### Biotransformations of Chlorophenols in Soil

When soil at old saw mill and wood preserving sites was analyzed, many more organic halogen compounds were found. The biodegradation of chlorophenols in soil, when degradable organic substrate is present, has been observed (18). Chlorophenol biomethylation is catalyzed by many soil organisms, both bacteria (25) and fungi (26). Since the resulting chloroanisols have a higher octanol–water partition coefficient, they are expected to be more mobile. Also, chloroanisols were observed to be more recalcitrant towards microbial mineralization than the parent chlorophenols (27,28). Therefore, biomethylation of chlorophenols into chloroanisols, by the indigenous or introduced microbes, is an undesirable activity and may even increase health danger. To remove danger, mineralization of the chlorophenols should be promoted. Organisms capable of catalyzing mineralization, also under in-field conditions, have been isolated and described (29–33). In field studies we detected chloroanisols in saw mill soils at quantities usually lower than those of chlorophenols (18). In contrast, we found that the major part of the soil at several saw mill sites contained solvent-extractable organic halogen (EOX) consisting not of chlorophenols or other small molecules but of much larger molecules. Figure 5 shows examples of molecular size distribution (MWD) of extractable organic halogens at two abandoned saw mill sites. The methods used to assay the MWD were the same as used earlier for pulp bleaching organic halogens.

As seen in Figure 5, size exclusion chromatograms reveal large sizes of organic halogens in soil. Such large molecules were not found (<0.001%) in the commercial formulation used at the mills. We found halopolymers in large quantity—from 50 to 500 mg of bound chlorine per kg of soil, depending on the site. Different soils exhibited different size distributions. Sandy, low-organic soils generally exhibited organic halogens eluting from 100 to 1000 g/mole (in Figure 5 exemplified by Kaustinen soil, pH 3.9, with ignition loss 7% w/w and EOX 120 mg/kg). Soils rich in organic matter eluted the main part of organic halogens in the range from 500 to 5000 g/mole (in Figure 5 exemplified by Toras soil, pH 6.3, with ignition loss 55% w/w and EOX 130 mg/kg).

The chlorophenolic compounds had thus become transformed into polymeric matter. The polymeric matter was chemically stable: hydrolysis at pH 10.3 and 82°C for 1 hr did almost nothing to the size distribution. Drastic hydrolysis, [3.75 M KOH in water–methanol 1:1 (v/v), for 30 min at 100°C] caused a shift of the Toras organic halogens into the area of molecular size near that found in Kaustinen soil before hydrolysis. We therefore conclude that the halopolymers contained covalently bound halogen. Our study revealed that, in old saw mill soils, extensive polymerization of chlorophenolics was taking place in situ, possibly catalyzed by enzymes or microbes present in soil. Coupling of chlorophenols to polymeric phenolic compounds by fungal oxidoreductive enzymes has been demonstrated in vitro and has been suggested as a potential bioremediative operation for chlorophenol-contaminated soils (34,35).

### Bioavailability of Large-sized Organic Halogens (Chlorohumus) in Soil

Polymeric organohalogen matter was found in the chlorophenol-contaminated soils. We used earthworms (Eisenia fetida andrei) as test animals to investigate bioavailability of the soil containing polymeric organic halogens.

Earthworms taken from kitchen compost were incubated in Toras and Kaustinen soils (Figure 5), with horse manure and water added to maintain the worms. After 12 and 25 days, respectively, the worms were collected, cleared of soil and worm feces, freeze dried, and solvent (tetrahydrofuran) extracted. Figure 6 shows the uptake of solvent soluble halogens from the soil by the worms. It shows that the exposed worms contained more organic halogen than the nonexposed worms and that organic halogen content of the worms incubated in sandy Kaustinen soil was extremely high.
The large soils content, generally significant, but was not so intensive as in the sandy soil. This was to be expected since the mobility of organic pollutants is generally known to depend on the organic matter content: the higher the organic content, the less mobile the chemical (36). The large amount of organic halogens accumulating in the worms from soil (concentration in worms was higher) indicate that most size classes of the chlorinated compounds present in soil may have bioaccumulation potential.

Figure 7 shows the molecular weight distributions of earthworm-accumulated organic halogens. The halogenated molecules in the earthworms were of very large molecular size, even larger than in the soils (Figure 5) in which they had been living. No such transition towards higher molecular weight was seen in the soil containing halo-organic matter during the residence time of the worms. Figure 8 shows the size distribution of organic halogens in the soils after the worms had been taken out; the distributions were very similar to those observed before the worms were introduced (Figure 5).

We conclude from these studies that the polymeric chlorohumus present in the saw mill soils was not bioinert, but it was bioavailable and it bioaccumulated into earthworms, hence possibly entering the food chain. It is therefore our opinion that promoting the bound residue production by fungi or their enzymes in soil may not be a safe protocol for bioremediating chlorophenol-polluted soils (37).

Biotransformations of Chlorinated Solvents in Soil and Human Exposure

Chlorinated ethenes are well-known pollutants of soil and groundwater in many countries. The reductive dehalogenous pathway of bacteria, leading from trichloroethenes and tetrachloroethenes to dichloroethene and, finally, to vinyl chloride has been known since the leukemia outbreak in the village of Woburn, Massachusetts. Our field studies revealed a case of serious trichloroethene and tetrachloroethene contamination of a groundwater well serving a rural community of 2200 people at Oittti in southern Finland in 1992 (38).

Figure 9 shows how the chlorinated ethenes had spread into village wells from the waste pit of an abandoned chemical cleaning shop. The village’s community water well contained 150 to 160 μg of the chloroethenes per liter. Also in this case, like that in Kärkölä, the polluter was located on a morene ridge, about 1000 m uphill from the community well. Figure 10 shows the subsurface findings near the chemical cleaning shop. The concentrations of vinyl chloride and 1,2-cis-dichloroethene were extremely high and exceeded those of trichloroethenes and tetrachloroethenes 1000-fold. Both the vinyl chloride and the dichloroethene have been products of microbial transformation in soil since neither chemical had been used in the village. Health studies are ongoing in this village, and no indications of health damage have yet been made public.

At another site in southern Finland, a heavy leakage of vinyl chloride and dichloroethene into groundwater was detected in 1974. Subsequently, the same chlorocarbons were detected in the wells of two villages (39). Concentrations of 5 to 200 mg of the chlorocarbons were measured in ground water in the mid-1980s. The origin of the leak was the waste liquor basin of an industry producing PVC and vinyl chloride. The researchers of the National Cancer Registry, unaware of any

400 to 800 mg Cl/kg, which is an order of magnitude higher than the soil concentration of solvent extractable halogen.

Figure 6. Molecular size distributions of halogenated (bars) and UV-Vis absorbing (lines) compounds extracted with tetrahydrofuran from the soils (Toras and Kaustinen) where the earthworms had been residing for 12 days. AU, absorbance unit. Worms were taken out before soil extraction. Mortality of the worms during soil exposure was 14% in Kaustinen soil and 16 to 24% in Toras soil. Analysis as in Figure 1.

Figure 7. Molecular size distributions of halogenated (bars) and UV-Vis absorbing (lines) compounds extracted with tetrahydrofuran from earthworms after residence in contaminated saw mill soils (Toras and Kaustinen) for 12 days. AU, absorbance unit. Analysis as in Figure 1.

Figure 8. Tetrahydrofuran-extractable organic halogen concentrations in (A) earthworms (*Eisenia fetida andrei) exposed to contaminated saw mill soils (Kaustinen and Toras) for 0, 12, and 25 days and in (B) the saw mill Kaustinen and Toras soils after housing the worms for 0, 12, and 25 days.
environmental pollution in the area, published a report on the unexplained excess of chronic lymphatic leukemia in the 1980s in the same community (40). Later, polychlorinated dioxins and polychlorinated furans were detected in soil in the same area, an estimated total of 120 g of 2,3,7,8-TCDD equivalents (22). The relationship of the various pollutants to residential health remains to be seen.

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