Sources of Organic Halogens in Spruce Forest Soil

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It is known that large amounts of organic halogens are present in soil, but the relative contribution from different sources is unclear. The aim of the present study was to determine the storage of organic halogens in a spruce forest soil and the deposition by needle litterfall and to elucidate the relative contribution from needle litterfall in relation to other sources and sinks. Sampling was conducted in a small spruce forest area in Denmark. Soil samples were collected at six locations to a depth of 60 cm. Litterfall was collected in 15 sample collectors every third month during 1 year. Soil leachate was collected below the B_h horizon over two periods of 5 days at five locations distributed over the study site. Throughfall data was compiled from a previous study conducted at the same site and during the same period as the present study, and data concerning net formation in soil was estimated from previous studies at similar sites. The pool was 630 kg of Cl_{org} ha^{-1}, contribution from litterfall was 0.35 kg ha^{-1} yr^{-1}, and loss by leaching was 0.63 kg of Cl_{org} ha^{-1} yr^{-1} (mean values). The estimated contributions from throughfall and net formation within the soil were 0.38 and 0.36 kg of Cl_{org} ha^{-1} yr^{-1}, respectively. The results suggest that the pool in the investigated soil originates mainly from sources within the forest and that it increases with time.

Introduction

The past years of research have shown that large amounts of organic halogens are present in the environment and that a considerable amount originates from natural sources (*1*). A major pool is found in soil, and there is evidence that halogens are natural constituents of soil organic matter, present in concentrations of 0.1–5 mg of Cl_{org} g^{-1} dw (*2, 3*). It has been shown that inorganic halogens are incorporated into the organic matter during decomposition, which suggests that natural formation in soil is one possible source (*4, 5*). Other possible (natural or anthropogenic) sources are precipitation and litter, which contain organic halogens in typical concentrations of 2–10 μg of Cl_{org} L^{-1} and ~0.1 mg of Cl_{org} g^{-1} dw, respectively (*6–9*). However, the relative contribution from these or other sources is not well known.

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The natural biogeochemical cycling of chlorine is practically a new field of research, which in itself makes it an interesting research area, especially as it seems like the formation of organic halogens in soil is related to the turnover of soil organic matter and to the carbon cycle (*5, 10*). In addition, many anthropogenic organohalogen compounds have undesirable environmental effects, and such compounds have, as a group, received considerable attention in the environmental debate for more than 30 years. As we now are learning that organic halogen compounds are formed and degraded naturally, it is becoming necessary to relate the occurrence of specific anthropogenic compounds to the natural biogeochemical cycle of such compounds. Therefore, the need to increase the understanding of the fate, effects, and cycling of anthropogenic organic halogen compounds demands an increase in the understanding of the natural background levels and processes. Hence, the biogeochemical cycle of organic halogens requires attention not only because it is a new field of research or because of its possible relationship to the turnover of organic matter but also because of its relationship to the cycling of anthropogenic organic halogen compounds.

The aim of the present study was to determine the storage of organic halogens in a spruce forest soil, to estimate the deposition by litterfall, and to elucidate the relative contribution from these sources in relation to deposition by throughfall and an estimated net formation within the soil.

Note on Terminology. Throughout the text, we use the term organic halogens, but the amount of organic halogens is quantified as the amount of chlorine for the following reason. When the total amount of organic halogens is determined, these elements are transferred as halide ions to a cell containing a solution of silver ions. The current (mA) used to re-establish the silver ion content of the cell after titration is proportional to the number of moles of halides added to the solution. Such a system detects chloride, bromide, and iodide but cannot distinguish between the different halides. Normally, chlorine is by far the most abundant halogen in environmental samples; hence, the total mass of halogens is, by tradition, calculated as the amount of chlorine (mg of Cl g^{-1} dw), as was done in the present study. Nevertheless, it should be kept in mind that since chlorine has a lower molecular mass than bromine and iodine, this methodology will result in an underestimation of the mass of organic halogens if the other halides are present in considerable amounts.

Sampling Procedures

Litterfall. In order to collect samples representing the heterogeneity of the needle litterfall, 15 sample collectors were randomly placed in the area (Figure 1). Sampling was conducted every third month, and the samples were collected in plastic bags, deep-frozen, transported, and stored at −20 °C until further treatments were conducted. The litter was then dried at 105 °C for 24 h and weighed. Twigs, cones, and, on a few occasions, trash were removed since influence from such litter would bias the results due to the immense variability of such litterfall as compared to the attainable sampling devices. The weight of the remaining needle litter was determined. The needle litter was then ground and sifted through a 0.1-mm mesh sieve, and the total amount of organic halogen (TOX) was determined in the samples.

Soil. Soil samples were collected on May 10, 1993, at six locations on an east–west line from the center to the edge of the forest (Figure 1). This was done in order to elucidate if the wind direction and distance from the forest edge would
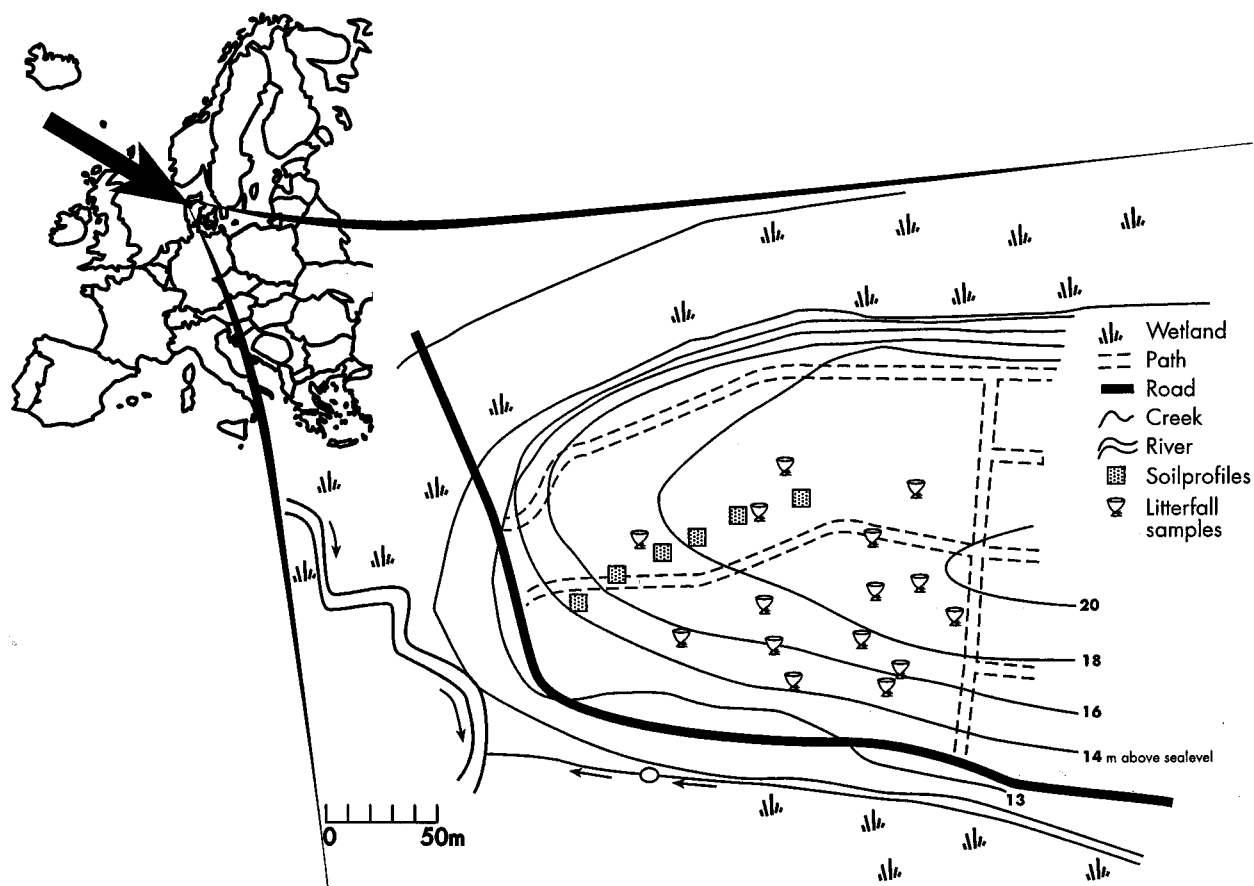
FIGURE 1. Key map showing the location of the Klosterhede Plantation on NW Jutland in Denmark (56°28′ N, 8°24′ E), including a map over the study site in the plantation.

influence the organic halogen pool. At each location, the entire soil core was collected to a depth of 60 cm. The samples were divided into 10 cm long subsamples, collected in plastic bags, deep-frozen, transported, and stored at -20 °C until further treatments were conducted. The samples were then dried at 105 °C for 24 h, weighed, sieved (2 mm), ground, and sifted (0.1 mm), and the total amount of organic halogens (TOX) and organic carbon (TOC) was determined.

Soil Leachate. Soil leachate was collected over two periods of 5 days each in May through June 1993 at five locations distributed over the study site. Sampling was done below the B_h horizon (45–50 cm depth), and three porous suction cups (PTFE) equipped with Teflon sampling lines were used at each location. As sampling was done after the onset of the dry season, several sampling cups yielded no or only low-volume samples on one or both occasions. Therefore, samples from the same location and same period were combined in order to obtain sufficient volume for AOX (adsorbable organic halogen) and DOC (dissolved organic carbon) analysis. Overall, seven combined samples from below the B_h horizon were analyzed. The samples were preserved by the addition of HNO_3 (2 mL of concentrate) per liter of sample and stored cold (<10°C) until analyzed.

Chemical Analyses

All chemicals used were of analytical grade.

Organic Halogen. Dried, ground, and sifted soil and litter samples were analyzed for TOX according to Asplund et al. (11). Briefly, a sample (2–50 mg) is mixed with an acidic nitrate solution (25 mL, 0.2 M KNO_3, 0.02 M HNO_3) in an Ehrlenmeyer flask. The mixture is shaken for 1 h; thereafter, the procedure follows that of the AOX procedure described below. Blanks without addition of soil are used, the detection level of the instrument is approximately 0.002 mg of $Cl_{org}\,g^{-1}$ dw, and the coefficient of variation among replicates is less than 0.1 (s/x).

Throughfall samples (ca. 300 mL) were filtered through a 0.1-μm membrane (Sartorius cellulose nitrate) after they were defrosted. Thereafter, the samples were analyzed for AOX according to the standard procedure (12). Briefly, an acidic nitrate solution and activated carbon are added to 100 mL of a sample and shaken for 1 h. After that, the suspension is filtered, and the filter with the filter cake is combusted at 950 °C in a Euroglas organic halogen analyzer (model 84/85). The amount of hydrogen halides formed is then measured by microcoulometric titration with silver ions. Each analysis was conducted in duplicate. For samples containing 40–200 mL, a volume smaller than 100 mL was used in order to permit duplicate analysis. Eleven of the samples contained less than 40 mL after filtration and DOC analysis. As analyzing such low-volume samples results in a high detection limit, these were not analyzed for AOX. Soil leachate samples were analyzed for AOX using carbon adsorption, removal of inorganic halides, combustion, and microcoulometric detection on a Dohrmann DX-20 TOX analyzer according to a modified method dedicated to groundwater analysis (13). The detection limit is approximately 0.5–1 μg of Cl_{org}/sample and thus dependent on the sample volume. The coefficient of variation for replicates of aqueous samples is less than 0.1 (s/x).

Organic Carbon. Organic carbon in soil samples was determined according to Roberts et al. (14) as modified by Grøn (15, 16), where the total amount of organic carbon (TOC) is estimated as the sum of the acid-desorbable organic carbon (ADOC) and the nonacid-desorbable organic carbon (NADOC). Inorganic carbon was removed from dried and

ground soil samples by successive washes with nitric acid (2 M). The total amount of ADOC was determined in the supernatants after centrifugation, where inorganic and volatile organic carbon was purged and the remaining organic carbon determined by UV/peroxodisulfate oxidation and infrared detection on a Dohrmann DC 180 TOC analyzer. The organic carbon fraction not desorbable with 2 M nitric acid (i.e., NADOC) was determined by carbon analysis of the acid-washed, centrifuged pellet using a Leco CS-225 carbon–sulfur determinator.

The total amount of dissolved organic carbon in through-fall samples was determined after filtration (0.1 μm, Sartorius cellulose nitrate) in 10-mL subsamples by using a Shimadzu 5000 TOC analyzer. For soil leachate samples, inorganic and volatile organic carbon was purged from the acidified samples, and the remaining organic carbon were determined by UV/peroxodisulfate oxidation and infrared detection on a Dohrmann DC 180 TOC analyzer.

For organic carbon analysis of aqeous samples, detection limits (0.1–0.5 mg of C_{org} L^{-1}) were calculated from standard variations obtained for blind sample analysis (Milli-Q water), whereas the coefficient of variation (<0.05 (s/x)) was evaluated from the analysis of synthetic controls (glucose in Milli-Q water) with an adequate concentration (17). For carbon analysis of solid samples, blind and control samples were carbon-free quartz sand and Leco standard materials, respectively, yielding a detection limit of 0.05% TOC and a relative standard deviation of 0.01 (s/x).

Statistics

All statistical analyses were conducted on a 5% significance level ($P = 0.05$). As there is an obvious risk that data might not have been following a normal distribution, we used median values for the collectors when calculating typical *concentration* values. This procedure will reduce the influence of outliers if the data are non-normally distributed but will have no influence on the results if the data are normally distributed, as the median and the mean are then one and the same. However, mean values were used when calculating *deposition* values, since all data, including outliers, should have an equal weight in order to give a fair estimate in these calculations. In assessing the deposition from throughfall and litterfall, each collector was given equal weight.

Results

General Observations. The total precipitation in the year from May 10, 1993, to May 6, 1994, was 857 mm and thus close to the mean annual precipitation in the area of 860 mm (18). However, the climate in Denmark in 1993–1994 was, in general, slightly colder and wetter than normal (19). The mean throughfall collected at our site from May 10, 1993, to May 6, 1994, was 590 mm, indicating an evaporation in the canopy zone of at least one-third of the annual precipitation. The study site, which is situated in a small spruce forest area in western Jutland, Denmark (56°28′ N, 8°24′ E), is described in detail elsewhere (20). The site is on a glacial outwash plain from the last glaciation with a typical humus-iron podzol (Orthod) developed on a sandy soil (21).

Quality Assurance. Analytical perfomance was ensured by participation in national Danish and Swedish interlaboratory comparisons (AOX and DOC) for the methods used for aqeous samples and in an international method study for TOC of soils.

Organic Halogens and Organic Carbon in the Soil. The median concentration of organic halogens in the soil samples was 0.13 mg of Cl_{org} g^{-1} dw, and the median organic carbon concentration was 58 mg g^{-1} dw (Table 1). The organohalogen pool stored in the upper 60 cm of the soil was estimated to be 630 kg of Cl_{org} ha^{-1}, and the pool of organic

TABLE 1. Concentration of Organic Halogens and Organic Carbon in Needle Litter, Soil, and Soil Leachate Collected in a Spruce Forest Soil in the Klosterhede Plantation, NW Denmark

	concn of organic halogens (μg of Cl_{org} dw^{-1} or L^{-1})		concn of organic carbon (mg of C_{org} dw^{-1} or L^{-1})	
	median	min–max	median	min–max
needle litter	101	51–196	ca. 500[a]	
soil	133	67–180	58	13–95
soil leachate	185	70–250	13	5.3–20

[a] Not determined.

carbon was estimated to be 180 ton of C_{org} ha^{-1} (Table 2). No influence on the pool of organic carbon or organic halogens in relation to the forest edge (and wind direction) was discernible among the six sampling locations.

Litterfall. The amount of litterfall varied among the collectors from 0.4 to 4.5 ton ha^{-1} yr^{-1}, with a mean value of 2.8 ton ha^{-1} yr^{-1}. Needle litter made up 77–99% of the total amount of the litter, giving a deposition of needle litter of 0.4–4.3 ton ha^{-1} yr^{-1} with a mean deposition of 2.41 ton ha^{-1} yr^{-1}. The median organohalogen concentration in the needle litter was 0.102 mg of Cl_{org} g^{-1} dw (Table 1). The estimated *amount* of organic halogens in the samples was linearly correlated to the amount of needle litter ($r^2 = 0.69$), whereas no relationship was seen between the *concentration* of organic halogen and the amount of needle litter. The deposition of organic halogens by needle litter was estimated to 0.35 kg of Cl_{org} ha^{-1} yr^{-1} (Table 2). Assuming that 50% of the needle litter consists of organic carbon, the deposition of carbon by needle litter was estimated to 1.2 ton ha^{-1} yr^{-1}.

Soil Leachate. The median concentration of organic halogens in soil leachate samples below the B_h horizon was 185 μg of Cl L^{-1}, and the median concentration of dissolved organic carbon was 13 mg of C_{org} L^{-1} (Table 1). The annual leaching of organic halogens and organic carbon from the B_h horizon can be roughly estimated. First, we assume that 40% of the annual precipitation is leached through the upper meter of soil, which is the general pattern in the temperate region (22) (i.e., 340 mm constituted the percolation). Second, we assume that the concentration values found in the soil leachate samples are typical for the investigated soil. This renders an annual leaching from the B_h horizon of 0.63 kg of Cl_{org} ha^{-1} yr^{-1} and 0.045 ton of C_{org} ha^{-1} yr^{-1} (Table 2).

Discussion

The present study shows that large amounts of organic halogens were stored in the investigated soil. The pools of organic halogens and organic carbon in the upper 60 cm of the soil were estimated to be 630 kg of Cl_{org} ha^{-1} and 180 ton of C_{org} ha^{-1}, respectively, with the sampling locations showing the lowest and highest pools differing by a factor of approximately 2. Thus, although the study was conducted in a comparably small and homogeneous study area, both the amount of organic halogens and organic carbon varied considerably among the six profiles. The same was observed for the deposited organic halogens and organic carbon among the 15 litterfall samplers. The variation recorded in our study stresses the point that many authors before us have pointed out: variation in natural environments is large, and this must be kept in mind when generalizations such as those appearing later in this paper are made. Still, the pool of organic carbon found here for a Danish forest (180 ton of C_{org} ha^{-1}) is in the same order of magnitude as the estimated organic carbon content in the upper 150 cm of Swedish forest soils of 158 ton of C_{org} ha^{-1} (23) and to the mean carbon content of temperate evergreen forest soils in the world, which is estimated to be 134 ton of C_{org} ha^{-1} (24).

TABLE 2. Pool of Organic Halogens and Organic Carbon in the Upper 60 cm in Soil and Fluxes of Organic Halogens and Organic Carbon in Needle Litterfall, Throughfall, and Net Formation within the Soil[a]

		organic halogens (kg of Cl_{org} ha^{-1})		organic carbon (ton of C_{org} ha^{-1})	
		median	min−max	median	min−max
pool in soil		630	490−800	180	150−310
sources (annual)	litterfall	0.35	0.40−0.69	1.2	0.2−2.2
	throughfall	0.38	0.064−0.91	0.051	0.01−0.13
	net formation in soil	0.36			
sink (annual)	leaching	0.63	0.24−0.86	0.045	0.02−0.07

[a] The data on throughfall are obtained from a previous study conducted at the same site and sampling period as the present study (*20*); data concerning net formation in soil are estimated from previous studies at similar sites (*5, 25*).

Relative Contribution from Different Sources and Sinks. The organic compounds present in a forest soil originate from vegetation, atmospheric deposition, direct anthropogenic sources (e.g., pesticide application or waste deposition), and intrinsic, natural formation within the soil. In addition to these sources, a number of sinks, such as uptake in the vegetation, degradation, leaching, and volatilization will influence the pool. For organic halogens in forest soils, the results of the present study, in combination with data from the literature, make possible a rough estimate of the relative contribution from different sources. The change in the pool (ΔCl_{org}) can be expressed as

$$\Delta Cl_{org} = Tf + Lf + A + nF - L - V - U$$

where ΔCl_{org} is the change in pool of organic halogens over time; Tf is the throughfall = wet deposition + dry deposition + canopy leachate; Lf is the litterfall; A is the direct anthropogenic sources to the soil; nF is the net formation in the soil, the sum of H (halogenation) and D (dehalogenation); L is the leaching from the soil; V is the volatilization from the soil; and U is the uptake in vegetation.

Below, we first discuss the relative contribution from litterfall and other sources and sinks to the pool of organic halogens in the investigated forest floor over the investigated year. Then we focus on the possibility of determining the change in the relative contribution from the sources and sinks over time.

Sources. The predominate source of organic carbon in a mature forest is Lf, and the annual litterfall in the present study corresponds to a little less than 1% of the total carbon pool in the soil (Figure 2). However, the deposition of organic halogens by litter only corresponds to about 0.04% of the organic halogen pool in the soil. This suggest that Lf contributes less to the pool of organic halogens than it does to the pool of organic carbon. Tf has been investigated in a previous study at the same study site and during the same time period as the present study (*20*). This study revealed that the deposition by throughfall was 0.06−0.91 kg of Cl_{org} ha^{-1} yr^{-1}, with a mean value of 0.38 kg of Cl_{org} ha^{-1} yr^{-1}, and 0.013−0.125 ton of C_{org} ha^{-1} yr^{-1}, with a mean value of 0.051 ton of C_{org} ha^{-1} yr^{-1}. The contribution from Tf to the overall carbon budget is generally negligible in comparison with Lf. Apparently, this was also the case in the present study (Figure 2). In contrast, the amount of organic halogens deposited by needle litter was slightly lower than that deposited by Tf, even though these two sources were in the same order of magnitude (0.35 and 0.38 kg of Cl_{org} ha^{-1} yr^{-1}, respectively).

No pesticides or wastes were applied at the field site during the study period, and to our knowledge, this had never been done before. Consequently, direct anthropogenic sources (*A*) need not be considered here.

The sum of formation and dehalogenation (nF) of organic halogens in the soil has been followed in previous studies as net changes in the content of organic halogens in decom-

posing spruce needle litter (*5, 25*). The annual net formation rate (nF) in these studies was about 50 μg of Cl_{org} g^{-1} of the original litter (i.e., 50 g of Cl_{org} ton^{-1} original litter) until 30−40% of the litter mass was lost (i.e., about 3−4 years of incubation); thereafter, the rate decreased rapidly to about zero. In the present study, the mean annual needle litterfall was 2.41 ton ha^{-1}. If we assume that a net formation takes place for 3 years at a rate of 50 g of Cl_{org} ton^{-1} y^{-1} and then goes to zero and that the litterfall was of the same size the preceding 3 years, the nF during the investigated year would have been 0.36 kg of Cl_{org} ha^{-1}. The net change in the organic carbon pool of the soil was not followed and cannot be estimated.

The estimated contributions of organic halogens from Lf, Tf, and an intrinsic net formation within the soil thus appears to be of approximately the same order of magnitude (Figure 2), and none of these sources are negligible in relation to the others. Overall, the input of organohalogens to the soil at the investigated site was estimated to be 1.1 kg of Cl_{org} ha^{-1} during the investigated year.

Sinks. In addition to the net formation of organic halogens in spruce needle litter observed previously (*5, 25*), net decreases were occasionally also found, implying that a dehalogenation (i.e., a release of inorganic halides) also may take place during degradation of spruce litter. Even though only nF, i.e., the sum of halogenation and dehalogenation, is given in Figure 2, the process of dehalogenation deserves a few words of reflection since it might constitute an important sink of organohalogens in soil. It is well documented that a number of white-rot fungi are capable of degrading chlorinated pollutants (*26−29*), and studies of degrading organic matter have indicated that dehalogenation of organic halogens generally takes place in soil (*5, 25*). This suggests that both a dehalogenation and a formation of organic halogens take place during the turnover of organic matter but that the formation rate is higher than the sum of dehalogenation and leaching during the first 3 or 4 years of degradation. Besides the dehalogenation (release of inorganic halides) of organohalogens, L, V, and U might influence the pool of organic halogens in soil as sinks.

The annual L from the B_h horizon was estimated to 0.63 kg of Cl_{org} ha^{-1} yr^{-1} and 0.045 ton of C_{org} has yr^{-1}. Since soil leachate samples were taken only during one short period of time, the results of the present study do not permit detailed calculations of this sink, but a rough estimate can still be done. Furthermore, comparisons with literature data support the accuracy of the estimations. The loss of organic carbon from soil by leaching has been determined at various sites. For example, McDowell and Likens (*30*) have studied DOC fluxes during passage through the forest floor in the Hubbard Brook Valley in New Hampshire. They found a flux of 0.054 ton of C_{org} ha^{-1} yr^{-1} in the upper B horizon and 0.023 ton of C_{org} ha^{-1} yr^{-1} in the lower B horizon. The loss from Swedish forest soils has been estimated to be 0.030 (0.01−0.05) ton of C_{org} ha^{-1} yr^{-1} (*23*), and Collier et al. (*31*) found that the flux
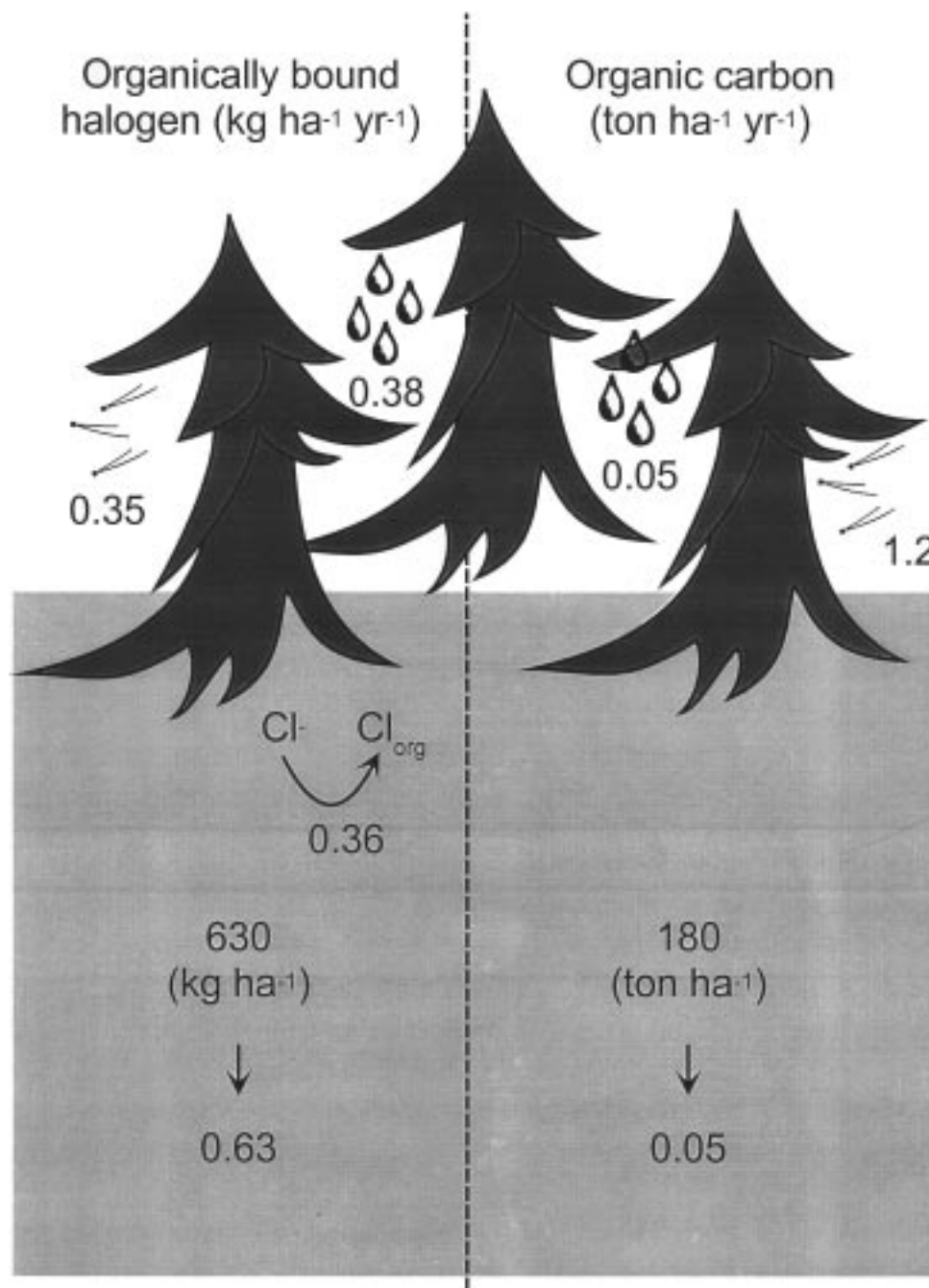
FIGURE 2. Overall picture of pools, sources, and sinks of organic halogens and organic carbon in the investigated spruce forest soil. The pools are given above the arrow at the bottom of the picture. The estimated sources are throughfall, needle litterfall, and net formation within the soil, and the estimated sink is leaching.

in some forested areas in New Zealand was 0.044−0.053 ton of C_{org} ha^{-1} yr^{-1}.

The present investigation did not encompass volatile organic halogens in the forest soil system. The method used to determine the amount of organic halogens in soil and litter involves drying the sample at 105 °C, and volatile compounds are thus lost (3). Furthermore, the special precautions that are necessary during sampling and analysis of organic halogens of throughfall and soil leachate, if volatile compounds are to be included, were not taken. Consequently, volatile compounds were not included in the organohalogen budget ($V = 0$).

There is virtually no information available concerning uptake of organic halogens by vegetation (U). However, the major part of the organic halogens in soil are bound to high molecular weight, humic-like substances (3), and it is generally believed that vegetation mainly takes up smaller compounds. It can therefore be assumed that uptake of organohalogens by vegetation is negligible in relation to other sources or sinks ($U = 0$), although it cannot be ruled out that this sink may influence the overall budget. Thus, the major sinks in the budget for the investigated area are leaching (0.63 kg of Cl_{org} ha^{-1} yr^{-1}) and perhaps dehalogenation, but the rate of this process is hidden by the formation processes that apparently proceed at a higher rate.

Change in the Pool over Time. The equation given above can be used for an estimate of the change in the pool over time. With Tf = 0.38, Lf = 0.35, $A = 0$, nF = 0.36, $L = 0.63$,

$V = 0$, and $U = 0$, all as kg of Cl_{org} ha^{-1} yr^{-1}, it is suggested that the sources of organic halogens in the investigated soil were larger than the sinks, which infers that the pool (ΔCl_{org}) ought to increase with time at a rate of not less than 0.46 kg of Cl_{org} ha^{-1} yr^{-1}.

The pool of organic matter in the temperate region has steadily increased since the last glaciation, and as halogens are apparently natural constituents of soil organic matter, it seems quite logical that the pool of organic halogens has also increased over the same span of time. Sources and sinks of organic matter change over time, both in the long term in relation to the overall climate and in the short term in relation to vegetational changes. Accordingly, the sources and sinks of organic halogens have most likely also changed over time. Though the data that are available concerning the biogeochemical cycling of organic halogens are quite scattered, a short reflection over the relative contribution from sources and sinks of organic halogens over time is worthwhile.

The amount of litterfall at the investigated site has increased from close to nothing during the years of clearfelling in 1946 to the 0.4–4.5 ton falling during 1993–1994. Consequently, the deposition of organic halogens by Lf has most likely also changed with the age of the stand, such that it has increased with increasing litterfall. H (incorporation of halogens) as well as D (release of halides) of organic matter in soil are relatively new and unexplored field of research, and previous studies focusing on these processes have all been conducted in comparably mature forests (3–5, 20, 25, 32–35). No studies have so far focused on differences among different time stages in a forest. Thus, it is not possible to assess the influence from this source/sink on changes in the pool over time.

Measurements of the total amount of organic halogens (AOX) in throughfall have been the focus of a number of studies, but in spite of this there are no time series available that last for more than 1 year. However, the use of chlorinated compounds has increased dramatically since the 1950s, and measurements of specific organohalogen compounds show that such compounds have increased during the last decades. This suggests that the concentration of the total amount of organic halogens in precipitation should be higher now than it was in preindustrial times, but only a minor fraction of the organic halogens in precipitation can be assigned to well-known pollutants, such as chlorinated solvents and pesticides, PCBs, and dioxins. The lion's share has hitherto not been structurally identified, and its origin is not known (8). Even less is known of the origin of organic halogens in Tf. However, more detailed examination on the Tf data suggests that the major part originates from internal sources within the forest (20). Still, no information is available concerning long-term temporal changes of any of the possible sources. Nevertheless, the deposition of gases, particles, and exudates will indeed increase as the canopies develop, and it therefore seems likely that the relative contribution by throughfall increases as the canopy cover increases.

Hence, the contribution from both Lf and Tf was previously most likely smaller than today, and it is therefore tempting to conclude that the nF within the soil was either underestimated in the present study or that it was larger in earlier days than it is today. However, the conclusions to be drawn concerning the relative contribution from different sources over time are that the relative contribution from Lf and Tf has probably increased with time or at least as the canopy cover has increased. The information concerning the influence of other sources (i.e., formation) and sinks (dehalogenation, leaching, and volatilization) on changes in the pool of organic halogens in soil is actually far too sparse to allow further conclusions to be made.

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