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Chloride and Organic Chlorine in Forest Soils: Storage, Residence Times, And Influence of Ecological Conditions

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Ⓢ Supporting Information

ABSTRACT: Recent studies have shown that extensive chlorination of natural organic matter significantly affects chlorine (Cl) residence time in soils. This natural biogeochemical process must be considered when developing the conceptual models used as the basis for safety assessments regarding the potential health impacts of 36-chlorine released from present and planned radioactive waste disposal facilities. In this study, we surveyed 51 French forested areas to determine the variability in chlorine speciation and storage in soils. Concentrations of total chlorine (Cl_{tot}) and organic chlorine (Cl_{org}) were determined in litterfall, forest floor and mineral soil samples. Cl_{org} constituted $11-100\%$ of Cl_{tot}, with the highest concentrations being found in the humus layer ($34-689$ mg Cl_{org} kg^{-1}). In terms of areal storage ($53-400$ kg Cl_{org} ha^{-1}) the mineral soil dominated due to its greater thickness (40 cm). Cl_{org} concentrations and estimated retention of organochlorine in the humus layer were correlated with Cl input, total Cl concentration, organic carbon content, soil pH and the dominant tree species. Cl_{org} concentration in mineral soil was not significantly influenced by the studied environmental factors, however increasing Cl:C ratios with depth could indicate selective preservation of chlorinated organic molecules. Litterfall contributions of Cl were significant but generally minor compared to other fluxes and stocks. Assuming steady-state conditions, known annual wet deposition and measured inventories in soil, the theoretical average residence time calculated for total chlorine (inorganic (Cl_{in}) and organic) was 5-fold higher than that estimated for Cl_{in} alone. Consideration of the Cl_{org} pool is therefore clearly important in studies of overall Cl cycling in terrestrial ecosystems.
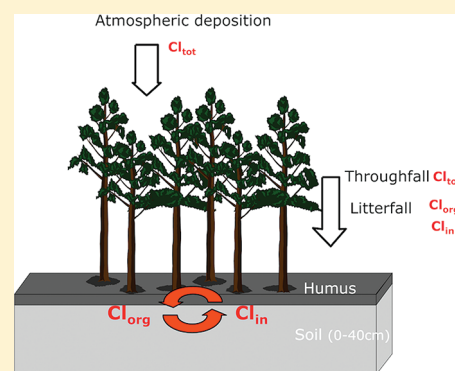
■ INTRODUCTION

Over the last 15 years chlorine biogeochemistry has become an important field of research in the context of nuclear power plant operation, spent nuclear fuel reprocessing and nuclear waste disposal.[1] The ^{36}Cl radionuclide formed within nuclear power plant reactors by neutron capture by the stable Cl present in the core, is a potential component of intermediate and high level radioactive wastes. Its high geochemical mobility and long half-life ($T_{1/2} = 3.01 \times 10^5$ years) make ^{36}Cl a critical radionuclide in nuclear waste disposal safety assessment.[2] The presence of the highly mobile and bioavailable ^{36}Cl$^-$ anion in soil columns may result in significant transfer to plants.[3] ^{36}Cl uptake by different edible plants and transfer to the food chain was shown to lead to high levels of human exposure.[4] Since ^{36}Cl can be considered to have the same behavior as stable Cl in soil and plants,[5] a good knowledge of stable chlorine behavior in various terrestrial ecosystems is necessary to adequately model ^{36}Cl transfer in the environment.

Chlorine is both widespread on Earth[6] and often considered as a conservative tracer of water movements in soil and subsurface environments, mainly because its inorganic anionic form (chloride, Cl$^-$, here also Cl_{in}) has low affinities for soil solid phases therefore allowing free movement between the various ecosystem components.[7] Nevertheless, this general view is open to question due to the thousands of known naturally produced organohalogens.[8−10] Indeed, many organisms are known to be able to produce chloro-organics in the biosphere. Interactions of Cl with biological organisms results in various chlorinated compounds being transformed, transported and degraded by means of a range of chemical or biochemical processes, resulting in a complex biogeochemical chlorine cycle.

In forest ecosystems, large amounts of Cl may be retained by organic matter.[11,12] Natural soil organic matter (SOM) chlorination processes occurring in forest soils were shown to be mediated primarily by microbial activities,[13,14] and there is even experimental evidence of abiotic chlorination of SOM.[15,16]

Production of organically bound halogens was reported to occur during biodegradation of lignin[17] through the action of litter-degrading fungi[18,19] and, more generally, by a majority of the basidiomycetes.[20]

Natural organochlorine production is proposed to be responsible for the occurrence of organically bound Cl (Cl_{org}) which is as abundant, or even more abundant, than the Cl_{in} pool in forest soils.[21,22] This natural chlorination will increase the average Cl residence time in the soil and thereby increase the exposure time following potential radiochlorine contaminations. In an attempt to construct a balanced chlorine budget for a small forested catchment in Sweden, Öberg et al.,[23] showed that the principal input and output fluxes of Cl are inorganic but that the main pool in soil is organic. This suggests significant Cl_{in} to Cl_{org} transformation (i.e., SOM chlorination), followed by subsequent leaching and degradation of Cl_{org} back to Cl_{in} (i.e., mineralization). Experimental evidence indicates that Cl_{org} formation and mineralization take place simultaneously in soil.[11,24] Equilibrium between these two processes is influenced by various environmental factors that are not as-yet clearly understood.[25,26] Some ecosystems may therefore act as a Cl^- source, while others act as a sink, but knowledge concerning the ecological conditions controlling the occurrence and degradation of chlorinated compounds in forest soils remains insufficient to explain changes in Cl storage. In fact, the distributions of Cl_{in} and Cl_{org} in soils are presently poorly understood, with only one large-scale spatial survey having been carried out for Cl distribution in the top soils (humus layers) in boreal forests in Southern Sweden.[27]

The goal of the study reported here, based on samples from the French Permanent Plot Network for the Monitoring of Forest Ecosystems (RENECOFOR) setup by the National Forest Board (ONF), was to quantify the Cl_{org} and Cl_{in} pools in forest soils under different climate and vegetation conditions, covering a greater variability than in the previous study and including not only the humus layer but also the "above-litter" and "below-mineral" soil layers. The data was used to estimate Cl pool sizes, net Cl_{org} formation rates in the humus layer, and Cl residence times in a variety of typical temperate forest ecosystems.

■ MATERIALS AND METHODS

Nature and Origin of the Studied Samples. Air-dried samples of litterfall, the forest floor (humus or organic layer) and the mineral layer (0–40 cm) of various forest soils were taken from the RENECOFOR collection.[28] The mineral and organic layers were sampled between 1993 and 1995 while the litterfalls were harvested in 1998. 51 forested sites were selected for our study, among them 27 sites equipped with weather stations. The studied sites are representative of the various forest types and climates of France. The survey concerns a range of different tree species assemblages found in deciduous to coniferous forests under different climate conditions (oceanic, transition, continental and mountain) leading to varying atmospheric deposition. According to the classification proposed in the Référentiel Pédologique,[29] the forest floor status at the different studied sites covered a large range of soil organic matter turnover, from easily degradable humus (Eumull) to recalcitrant humus (Mor).

Chlorine Measurements: Determination of the Organic Chlorine Pool. Dried samples were ground to a fine powder, and the total Cl (Cl_{tot}) contents in the litterfall, organic and mineral layers of each soil were measured by INAA (Instrumental Neu-

tron Activation Analysis) at the Reactor Institute of the University of Delft, Netherlands.

An extraction procedure based on Bastviken et al.[30] was performed to quantify the organic pool of chlorine (Cl_{org}) in all the samples. For each sample (litter, humus and soil from each site), 1.0 g of dry and ground matter were added in 35 mL Nalgene centrifuge tubes with 20 mL of deionized water and the tubes were placed on a shaker for 1 h. The tubes were then centrifuged at 15 000 rpm for 15 min and the supernatant transferred to a new flask. An additional 20 mL of deionized water were added to the residual matter. The suspension was sonicated for 45 s before shaking 1 h and centrifugation at 15 000 rpm for 15 min to yield a second water extract. This extraction procedure was repeated two additional times with 20 mL of an acidified potassium nitrate solution (0.1 M KNO_3, 0.02 M HNO_3), yielding extracts 3 and 4. The four extracts were filtered through a cellulose acetate/nitrate filter (0.45 μm) and pooled together. The residual matter in the centrifuge tube after the fourth extraction was resuspended in deionized water, then filtered through the same filter. The filtrate contained the extractable Cl (i.e., inorganic chlorine Cl_{in} and Cl associated to extracted organic matter Cl_{orgex}), while the residual nonextractable Cl remaining in the solid fraction was assumed to include at least 90% of the Cl_{org} of the sample.[30] In the following results, this non-extractable Cl is referred as the organic chlorine pool. The residual matter was dried in an oven at 40 °C for several days and then analyzed for Cl_{org} concentration by INAA (Reactor Institute of Delft). Cl_{in} was determined by difference between Cl_{tot} and Cl_{org} concentrations.

Additional Data and Calculations. A wide range data regarding soil physicochemical properties and climate conditions were collected, following a grid sampling protocol, by the RENECOFOR network allowing precise characterization of the studied sites.[28,31] In humus and surface soil, the C content was determined by measurement of CO_2 formed after combustion at 1030 °C (Dumas method). In deeper layers, the organic carbon was measured by a colorimetric method after oxidation with $K_2Cr_2O_7$ at 135 °C in acidic condition (Anne method, procedure AFNOR X 31-109).[31] When chlorine input (i.e., mean Cl atmospheric deposition in kg Cl ha^{-1} yr^{-1}) was known (for 27 sites), a theoretical average residence time of chlorine in soil (t_{resCl}) was estimated using the following formula:

$$t_{resCl} = \frac{\text{pool of chlorine in humus} + \text{mineral soil}}{\text{Annual atmospheric input of chlorine}} \text{ (years)}$$

This theoretical residence time was calculated assuming steady state based on (i) the inorganic components only (Cl deposition and Cl_{in}) yielding $t_{resClin}$, which represents the traditional view that Cl_{in} is nonreactive, and (ii) the Cl deposition and the total standing stock of Cl in the soil (Cl_{in} plus Cl_{org}) yielding $t_{resCltotal}$. While uncertainties regarding annual net input of Cl_{org} made calculation of the residence times of Cl subpools impossible, this limited approach provides a means of estimating the extent to which the Cl_{org} pool affects the total average Cl residence times in soil.

Net Cl accumulation rates in humus was also estimated as follows:

$$\text{Cl accumulation rate} = \frac{([Cl]_{humus} - [Cl]_{litter}) \times DM_{humus}}{t_{resDM}} \text{ (gClm}^{-2}\text{year}^{-1})$$

where $[Cl]_{humus}$ and $[Cl]_{litter}$ denote the total Cl concentrations
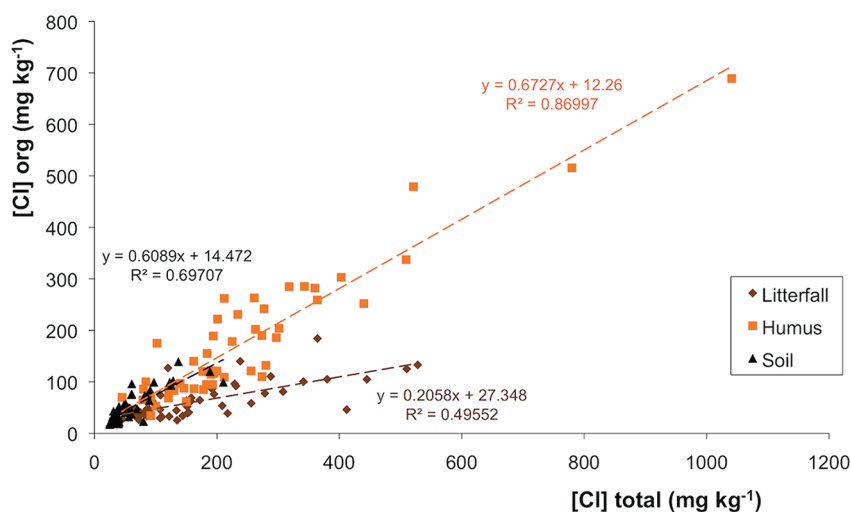
Figure 1. Concentration of organic chlorine as a function of total chlorine concentration in litterfall, humus and mineral soil of the studied sites.

(mass Cl per dry mass soil), DM_{humus} is the dry mass of the humus layer per m^2, and t_{resDM} is the average dry matter residence time in the humus layer. t_{resDM} was calculated considering the loss of litter due to mineralization before it turns into humus from the equation:

$$t_{resDM} = \frac{DM_{humus}}{LF \times (1 - \text{litter fraction mineralized})} \ (\text{years})$$

with DM_{humus}: humus dry mass ($kg\ ha^{-1}$), that is, the amount of dried forest floor harvested at the sampling time and calculated for one ha; LF: annual litterfall dry mass ($kg\ ha^{-1}\ year^{-1}$), that is, the total amount of dried litterfall harvested during the year of sampling and calculated for one ha; "litter fraction mineralized": the mass loss of litter due to mineralization before it is transformed to humus.

Some limit values for cumulative mass loss were reviewed by Osono and Takeda,[32] giving a range in European forests between 35 and 100%. In the calculation, we selected the average mass loss values for the different soils based on the dominating tree species studied: 85% in pines, 70% in douglas, 61% in spruce, 51% in silver ir, 65% in beech, and 43% in oak forests.

Statistical Analyses. Statistical analyses were performed using the FactoMineR package implemented within the R commander environment. The data were not found to be normally distributed, even after Log-transformation. Kruskal–Wallis rank sum tests and Kendall's correlation tests were thus applied to assess the effects of environmental factors.

■ RESULTS

Cl input: Cl atmospheric deposition vs Cl in litter. The atmospheric Cl inputs measured in open bulk collectors in tree-free areas nearby the studied sites, decrease from west to east (Supporting Information (SI) Figure S1) with sites closer to the Atlantic coast have mean annual Cl inputs greater than 23 kg Cl ha^{-1}, some stations having >50 kg Cl $ha^{-1}\ yr^{-1}$ (SI Table S1). In eastern France, where the oceanic influence is low, less than 6 kg of Cl ha^{-1} comes from bulk atmospheric deposition. A particular case is the station in Corsica, which is influenced by both mountain and Mediterranean climates.
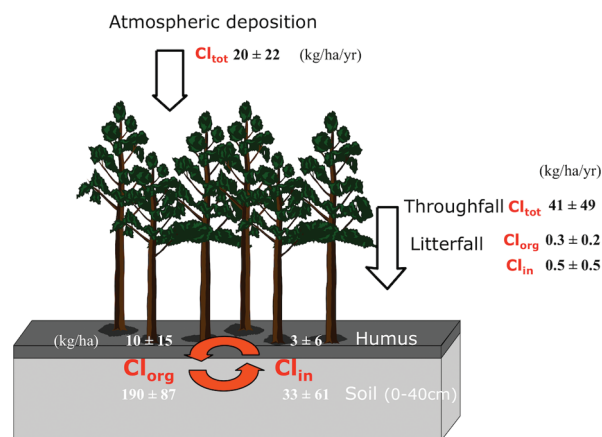

Figure 2. Chlorine budget in French forests (mean ± standard deviation; $n = 27$ for atmospheric deposition and throughfall values; $n = 51$ for the other means).

The concentration of total chlorine in litterfall varied between 46 and 530 mg kg^{-1} with a median value of 150 mg kg^{-1} and was not correlated to atmospheric Cl deposition (Kendall's rank coefficient $\tau = 0.23$, $p = 0.087$). Total Cl inputs through litterfall (0.1–2.5 kg Cl $ha^{-1}\ yr^{-1}$) were generally low compared to Cl in atmospheric deposition at most sites, but may be of significant importance in case where Cl atmospheric deposition is limited. Cl in litterfalls represented from 1 to 70% of inputs. Oceanic climate sites had total Cl inputs (atmospheric deposits + litter input) onto the topsoil ranging between 13 and 78 kg Cl ha^{-1} yr^{-1}. Transition climates gave a range of 7–25 kg Cl $ha^{-1}\ yr^{-1}$ and continental climates from 4 to 11 kg Cl $ha^{-1}\ yr^{-1}$. In mountain locations, total Cl input ranged from 3 to 20 kg Cl $ha^{-1}\ yr^{-1}$. According to Öberg et al.,[23] chlorine was considered to be present mainly as Cl_{in} in wet deposition. In litterfalls, 41 ± 18% of total chlorine was organic chlorine without any significant trends in Cl_{org}/Cl_{in} ratio.

Cl in Humus and Mineral soil. Total chlorine concentrations in humus (45–1040 mg kg^{-1}, mean and median values = 247 and 198 mg kg^{-1}, respectively) were in the same range as in litterfall, while concentrations in mineral soil were lower
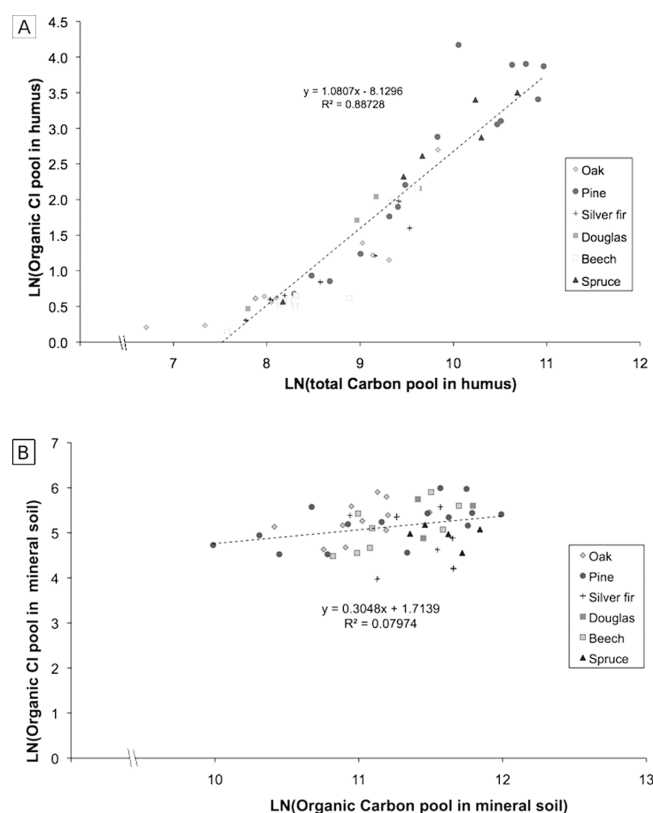
Figure 3. Pool of organic chlorine (kg Cl ha^{-1}, ln-transformed) as a function of the carbon pool (t C ha^{-1}, ln-transformed) in humus (A) and in mineral soil (0−40 cm) (B) in the studied forests.

Table 1. Differences in Cl$_{org}$ Standing Stocks According to Classes of Environmental Factors (Tree Species, Climate, C Stock and Surface pH), Assessed with Kruskall-Wallis Rank Sum Tests^a

	Cl$_{org}$ standing stocks					
	Litterfall		Humus		Mineral Soil	
Factors	χ^2	p-value	χ^2	p-value	χ^2	p-value
Tree Species	27.435	0.00028 ***	23.550	0.0014 **	7.894	0.342 ns
climate	5.292	0.1517 ns	6.256	0.0996 ns	4.622	0.2017 ns
C stock		ND	44.22	1.36e-09 ***	3.166	0.3667 ns
pH$_{0-10\ cm}$		ND	19.115	0.00026 ***	6.456	0.0914 ns

^{a} ns: not significant at the 5% level, ** p < 0.01, *** p < 0.001. Different qualitative groups were defined for each factor: Oak, Douglas, Spruce, Beech, Maritime Pine, Scots Pine, and Silver-fir for tree species; oceanic, transition, continental and mountain for climate; low, low-medium, medium-high, and high for C stock and pH$_{0-10\ cm}$.

considering the retention of Cl$_{org}$ in soil increases the calculated Cl residence time by a factor of 5 as compared to Cl$_{in}$ alone, but it remained low compared to DM residence times in humus (1−333 years).

The calculated net Cl accumulation rates in humus ranged from −0.92 to +0.43 kg Cl ha^{-1} yr^{-1} depending on the dominant tree species in the forested sites (Kruskall-Wallis χ^2 = 17.47, p = 0.0077). Humus with negative accumulation rates, especially in oak and beech forests, indicates that Cl is lost from the humus layer. On the otherhand, observed positive accumulation rates (mostly in douglas fir, spruce, and pine forests) reflect retention of Cl and presumably a net accumulation of Cl$_{org}$ in humus compared to litterfall.

Influences of Pedoclimatic Conditions and Tree Species. The total and organic Cl concentrations in the humus layer were significantly higher under an oceanic climate than under transition, continental and mountain climates (Kruskal−Wallis χ^2 = 10.89, p = 0.028 for Cl$_{tot}$; χ^2 = 9.03, p = 0.029 for Cl$_{org}$). A weak correlation between total Cl concentration in humus and atmospheric Cl deposition was also found (Kendall's τ = 0.30, p = 0.029). Total Cl concentration in mineral soil (0−40 cm) was, on the other hand, not influenced by atmospheric chlorine deposition (χ^2 = 3.75, p = 0.441). Moreover, $t_{resCltotal}$ was significantly longer in inland sites than in coastal sites (χ^2 = 8.59, p = 0.035). Indeed, on the average, Cl residence time in soil and humus was 35 ± 19 years in inland sites, whereas it was 12 ± 7 years in coastal forests.

The dominant tree species was found to be a major factor influencing organic chlorine concentrations and pools. In this study, two groups of dominating tree species can be distinguished: oak, beech, and silver fir (O−B−S) with fast DM decomposition (t_{resDM} = 9.1 ± 8.6 years) on one hand, and pine, spruce and douglas (P−S−D) with slow DM decomposition (t_{resDM} = 106 ± 103 years) on the other hand. Organic chlorine concentrations were found to be significantly different between these two groups of tree species in humus (χ^2 = 16.80, p < 0.0001) but not in mineral soil 0−40 cm (χ^2 = 1.72, p = 0.1893) nor in litterfall (χ^2 = 1.89, p = 0.1690). In the humus layer, concentrations of Cl$_{org}$ were significantly higher in P−S−D forests (median value =222 mg kg^{-1}) than in O−B−S forests (98 mg kg^{-1}). However, chlorine residence times ($t_{recCltot}$) were not significantly different between these two groups of forests (χ^2 = 0.99, p = 0.32).

(25−210 mg kg^{-1}, mean and median value =62 and 48 mg kg^{-1}) (Figure 1, SI Table S2). Cl concentrations in litterfall and humus also showed a greater variability between sites than in the mineral soil layer. Significant positive correlations were found between organochlorine concentration and total Cl concentration in humus (Kendall's rank coefficient τ = 0.71, p < 0.001), in soil (τ = 0.64, p < 0.001) and in litterfall (τ = 0.53, p < 0.001) (Figure 1). On the average, Cl$_{org}$ accounted for 75 ± 27% and 89 ± 26% of the total Cl in the humus and mineral soil, respectively.

Mean chlorine inventories in the studied forested sites are shown in Figure 2. Despite higher Cl concentrations in humus and litterfall, the highest Cl pool was in mineral soil (0−40 cm) regardless of the forest ecosystem considered. The stock of organic chlorine in mineral soil ranged from 53 to 400 kg Cl$_{org}$ ha^{-1}, while there was between 0.2 and 64 kg Cl$_{org}$ ha^{-1} in humus.

The amount of Cl$_{org}$ in humus was highly correlated to the C content (Kendall's correlation coefficient τ = 0.84, p < 0.001), whereas there was no such correlation in mineral soil (Kendall's correlation coefficient τ = 0.20, p = 0.0474) (Figure 3). The chlorine-to-carbon ratios increased downward, ranging from 0.08 to 2.7 mg Cl$_{org}$ g^{-1} C in humus and from 0.6 to 6.1 mg Cl$_{org}$ g^{-1} C in mineral soil (0−40 cm), which is in the same range as in a previous study of spruce forest stands for which Johansson et al.[21] reported ratios from 0.76 to 3.75 mg Cl$_{org}$ g^{-1} C.

The average theoretical Cl residence times calculated for Cl$_{in}$ only ($t_{resClin}$) and for total Cl including Cl$_{org}$ ($t_{resCltot}$) were 4 and 22 years, respectively. $t_{resCltot}$ ranged from 3 to 67 years and was 5-fold higher than $t_{resClin}$ (0 to 14 years). This indicates that

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No relationships were observed between Cl_{tot} or Cl_{org} contents and such soil parameters as C/N ratio, CEC and %clay. Nevertheless, organic chlorine dynamics seemed to be influenced by soil pH, with Cl_{org} concentrations in humus tending to be higher at pH 4 and decreasing with increasing pH (SI Figure S2).

It is important to know which conditions influence the chlorine budget in forest soils, and especially those which determine wether the standing stocks of Cl_{org} are low or high. The main effects of environmental factors on the standing stocks of Cl_{org} are shown in Table 1. The annual stocks of Cl_{org} coming from the litterfall were significantly related to the dominant tree species but not to climate. Higher litter Cl_{org} stocks were measured in Oak forests as compared to the other tree species due principally to the higher litter dry mass and slightly higher Cl_{org} concentrations in Oak litterfalls. The Cl_{org} standing stock in humus was the most sensitive to environmental factors being significantly affected, at the 5% level, by the tree species, the carbon stock in humus and by surface pH. The Cl_{org} standing stock in mineral soil, on the other hand, was not significantly dependent on the tested factors. In humus, the Cl_{org} stocks were highest in Maritime and scots pines forests and lowest in oak, beech, and silver fir forests. Cl_{org} stocks were higher in forests with large carbon stocks in humus and with low surface pH. It also tended to be affected by climate (significant at the 10% level).

■ DISCUSSION

This study provides a large-scale view of chlorine content and distribution patterns in soils of temperate forested ecosystems. In agreement with previous studies, it highlighted the important role of forests in Cl cycling. A substantial amount of organic chlorine, defined as nonextractable Cl following a well-established procedure, was present in the topsoil of different forest ecotypes. The capture of Cl in soil as a result of OM chlorination processes resulted in a stock of 0.2 to 64 kg Cl_{org} ha^{-1} in humus and 53−400 kg Cl_{org} ha^{-1} in the first 40 cm of mineral soil. These values, measured on a large set of French forest soils, are in the same range as those estimated in Swedish forests (∼130 kg Cl_{org} ha^{-1}),[22,23] and slightly lower than the organic Cl storage (630 kg Cl_{org} ha^{-1}) found by Öberg and Grøn[33] in a spruce forest soil (0−60 cm) in Denmark. However, the Cl pool stored in mineral soil was much higher than the Cl in humus, and was certainly even higher than the calculated value since most soils are deeper than 40 cm.

Regarding organic chlorine concentration, our results are comparable to that reported in the only available work investigating Cl occurrence in a large mixed forested area. In that study, Johansson et al.[27] measured lower organic Cl concentrations in the O-horizon of deciduous forests relative to that in coniferous forests, and they found that Cl_{org} formation in soil correlated with Cl_{in} deposition. These findings were partly confirmed by our observations, wherein Cl_{org} concentrations in humus were found to be significantly higher at sites with a thick organic layer, that is, especially in douglas, spruce and pine coniferous forests, as compared to oak, beech, and silver fir forests. Silver fir (*Abies alba*) is a coniferous species which has a forest dry matter decomposition pattern closer to deciduous than coniferous forests. The dominant tree species seemed to be a key parameter influencing Cl_{org} storage in soils. This parameter, in addition to the atmospheric Cl input, significantly influenced Cl accumulation in humus. On the other hand, the larger Cl pool, i.e. that retained in mineral soil, was not significantly different among forest types or

climates. It remains to determine whether active OM chlorination may occur in mineral soil or if the organochlorines in this 0−40 cm layer was simply leached from the upper organic layer. In general, there is still a poor understanding of the mechanisms behind the formation, mineralization and transport of organic chlorine in forest soil profiles.[23,25,26] In a spruce forest soil, Öberg[11] showed that the chlorine-to-carbon ratio increases from the organic layer to the underlying mineral horizon, a finding confirmed by our results for various forest soils. A large number of microorganisms, most of them plant material decomposers[34] have the ability to form low molecular weight (LMW) chlorinated compounds.[10] On the other hand, high molecular weight (HMW) organic compounds (>10 000 g mol^{-1}) were found to constitute up to 50% of the chlorinated organic pool in deeper soil.[12] This suggests that LMW chlorinated organic compounds are formed predominantly in surface organic layer and then leached to lower soil where it becomes either integrated in HMW organic compounds or subject to further halogenations.[35] An alternative to continued chlorination in the mineral soil is selective preservation of some Cl_{org} relative to average SOM, a hypothesis supported by the independence of Cl_{org} and organic carbon levels in the mineral soil. Non-negligible amounts of Cl_{org} (40% of total Cl) were also measured in litterfalls, which means that a transformation of Cl_{in} in Cl_{org} occurs before plant materials reach the ground. It is still unclear, however, whether chlorination processes occur within plant cells, on leaf surfaces, or both.

Recent experiments demonstrated that organic chlorine formation in forest soils is largely mediated by microbial activities through the action of enzymes,[30,14] which explains the spatial and temporal variability of the chlorination process. Enzymatic activities depend on the abundance of the substrate available for the reaction, for example, the content of organic carbon molecules and inorganic chlorine in the case of the chlorination reactions. Enzyme action is also pH-dependent, which may explain why organic chlorine concentrations tended to be higher in soils having pH values around 4, the highest organic C contents and high total Cl concentrations. Spatial heterogeneity is a common aspect affecting organic matter and soil studies which, coupled with the fact that humus and soil samples were collected at different periods of the year, may have enhanced result variability. For example, Johansson et al.[27] found that Cl_{org} concentration varies seasonally, with a decrease of Cl_{org} from June to August followed by a tendency to increase in September/October. An increase in microbial activity in autumn was proposed to be the cause of higher chlorination of organic matter at this period leading to higher chlorine-to-carbon ratios.[36]

Obviously, the pools of Cl_{in} and Cl_{org} in forested soils are not static. The dynamics could be driven by the atmospheric Cl inputs and by both OM chlorination and mineralization processes. In surface organic layers, the calculated long-term net Cl accumulation rates were based on measurable changes in Cl concentrations during degradation of plant litter (from litterfall to humus). Therefore these values must be interpreted as trends in the organic chlorine pool over many years. Such a change was estimated by Öberg and Grøn[33] to be around +0.5 kg of Cl_{org} ha^{-1} yr^{-1} in a spruce forest soil. Our results were lower for similar forest types and showed that, in other cases, the soil organic layer acted as a source of chloride since the Cl accumulation rates reached negative values. This is in agreement with imbalances reported in a short-term lysimeter experiment, where some lysimeters acted as a sink of Cl_{in} whereas others were sources of Cl^-.[35] In soils with negative net Cl accumulation,

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mineralization of Cl_{org} initially present followed by removal of Cl_{in} could have been predominant over the OM chlorination process, providing a possible explanation of observed short-term patterns. Long-term net release of Cl is however more likely to be explained by a lack of information about Cl sources such as deposition of Cl_{org} or Cl contributions from weathering.

Although evidence of Cl association with organic matter has been widely documented in the literature, the impact of such association on the persistence of Cl in the soil profile of contrasting forest types is not known. One aim of this study was to estimate chlorine residence times in soils. We found an average value of 22 years, which is in agreement with Cornett et al.[37] who studied the cycle of ^{36}Cl from weapons test fallout in Eastern North America. They estimated a Cl residence time of 20 years in soil and at least 25 years in the terrestrial biosphere. Bastviken et al.[24] estimated a total turnover time of soil Cl_{in} of the order of 1−10 years in a Swedish coniferous forest soil, related to Cl_{org} formation. Our results also highlighted the importance of chlorine retention as organochlorine in the residence time calculations. Chlorine retention time was indeed shown to be 5-fold higher when taking Cl_{org} into account. However, it should be noted that the calculated residence times represent averages for several widely different pools of Cl, some of which having a very short residence time (Cl_{in}), and others a range of residence times from intermediate to perhaps very long if there is selective preservation of Cl_{org} relative to average SOM in soils. As a comparison with other radionuclides characterized by a low mobility in soil, Bunzl et al.[38] reported residence half-times of radiocesium from global fallout of about 15 and 100 years in organic (Of-Oh: 7 cm) and underlying mineral (Ah: 5 cm) layers of a spruce stand. For plutonium global fallout, Frissel et al.[39] estimated residence half-times between 1 and 3 years cm^{-1} for several soils from The Netherlands and Germany, which is also similar to that observed for plutonium in a spruce forest.[40] From these residence half-times, we deduced residence times values of 108 and 721 years for cesium in organic and mineral layers, respectively, and 289−866 years for plutonium, which is much longer than the 22 years calculated for average chlorine ($Cl_{org} + Cl_{in}$). It is possible that recalcitrant fractions of Cl_{org} could have residence times comparable to those of cesium and plutonium, with the increasing Cl:C ratio with soil depth indicating selective preservation of some Cl_{org} fractions. Our residence time calculations assume steady state conditions where input is similar to output. The residence time calculations are therefore very sensitive to Cl input, which can explain the difference between coastal and inland sites. The net accumulation in the humus layers ranging from −112% to +10% of the storage also indicates that steady state may not be the case. Therefore the residence time calculations should be considered as rough estimates and an illustration of the importance of taking Cl_{org} into consideration. In addition, the similarity of the calculated residence times among sites with widely different vegetation and Cl_{org} levels could indicate similar behavior of the Cl_{org} regardless of where it is formed.

In conclusion, the biogeochemistry of chlorine in temperate forests is a particular case that must be taken into account when carrying out radioactive waste safety assessments. It is clear that radiochlorine can be retained in soils, and that this process will be influenced by environmental conditions. The data set used in this study tends to indicate that the organic layer (humus) appears to be the most active part of the soil profile in terms of this retention. Cl storage in humus depended on Cl input (climate), tree species, carbon content and soil pH, while Cl in mineral soil seemed to be more stable over a range of pedoclimatic conditions. In general, coniferous forests with a slow organic matter turnover in soil showed most Cl accumulation in an organic form.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Two tables of the characteristics of the studied stations. A map of the French climates with chlorine atmospheric deposition in studied sites equipped with weather station (Figure S1) and a figure of the relationship between surface pH and percentage of Cl_{org} in humus (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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