Iodine budget in forest soils: Influence of environmental conditions and soil physicochemical properties

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HIGHLIGHTS

- Measurement of I concentrations in French forest soils (litterfall, humus and soil).

- Rainfall iodine concentrations probably influenced those of litterfall.

- Throughfall was the major iodine input to soils compared to litterfall.

- Major role of organic matter, iron and aluminium in iodine persistence in soils.

- Concentrations of I in forest soils varied with vegetation and climatic conditions.

- Keywords: Iodine, Forest, Soil, Residence time, Environmental conditions

ABSTRACT

Due to its longevity, radioisotope ^{129}I is a health concern following potential releases in the environment which raises questions about residence and exposure times relevant for risk assessments. We determined ^{127}I concentrations (as a surrogate for ^{129}I) in a series of French forest soils (i.e. litters, humus and mineral soils) under different vegetation and climate conditions in order to identify the major processes affecting its accumulation and persistence in the soil column. The input fluxes linked to rainfall, throughfall and litterfall were also characterized. Main results obtained showed that: (i) rainfall iodine concentrations probably influenced those of litterfall through absorption by leaves/needles returning to the ground; (ii) throughfall was the major iodine input to soils (mean = 83%), compared to litterfall (mean = 17%); (iii) humus represented a temporary storage of iodine from atmospheric and biomass deposits; (iv) iodine concentrations in soils depended on both the iodine inputs and the soil's ability to retain iodine due to its organic matter, total iron and aluminium concentrations; (v) these soil properties were the main factors influencing the accumulation of iodine in the soil column, resulting in residence times of 419-1756 years; and (vi) the leaching of iodine-containing organic matter dissolved in soil solution may be an important source of labile organic iodine for groundwater and streams.

1. INTRODUCTION

Exposure to radioisotopes of iodine (I) targeting the thyroid gland is a health concern, most notably following major nuclear accidents (e.g. Chernobyl and Fukushima). Moreover, the radioisotope 129I ($t_{1/2}$ = 15.7 10^6 years) has received considerable attention because of its presence in high-level and long-lived radioactive waste. Thus, a better understanding of the long-term processes controlling iodine biogeochemistry in the environment is necessary.

Natural iodine, composed of the stable isotope ^{127}I and the longlived ^{129}I, is a trace element in the environment. Igneous rocks contain less iodine than sedimentary rocks (mean = 0.24 and 2.0 mg kg^{-1}, respectively), and most soils contain more iodine than the bedrocks and sediments from which they derive (mean = 5 mg kg^{-1}) (Christiansen et al., 1989; Fuge and Johnson, 1986; Johnson, 2003). Furthermore, it is widely accepted that soil iodine largely originates from the oceans due to its volatilisation into the atmosphere (Fuge and Johnson, 2015). Iodine concentrations in soils result from several processes such as retention and leaching. Iron (Fe), aluminium (Al) and manganese (Mn) (hydr) oxides in soils can play an important role in iodine sorption as well as soil organic matter (OM) (Bowley, 2013; Shetaya et al., 2012). Since forest soils contain large amounts of OM, they could be an important iodine terrestrial sink. Limited data is available on iodine distribution in forest trees and soils (Bostock, 2004; Korobova, 2010; Muramatsu et al., 2004; Takeda et al., 2015; Xu et al., 2016). In our previous study which focused on a Beech forest (Roulier et al., 2018), soil was the larger iodine pool and its uptake by trees was limited (<0.2% of the available iodine pool in soil). Litterfall was a major pathway in the iodine biological cycling but a lower iodine input to soil than atmospheric depositions. Although vegetation did not appear to be a major factor in iodine recycling, the high turnover of OM in forests could promote conditions for iodine accumulation and persistence in forest soils. These conclusions were obtained from a specific beech forest site. However, iodine inputs and their persistence in forest soils may vary with ecological conditions.

The goals of this study were (i) to quantify iodine concentrations and stocks in French forest soils (i.e. litterfall, humus and mineral soils) under different climate and vegetation conditions, (ii) to estimate the net iodine accumulation rates in the humus layer and the iodine residence times in humus and soil and (iii) to identify the environmental conditions that influence the iodine budgets in these soils. Hereafter, 'environmental conditions' is used to designate tree species, humus, soil, climate and geological formation types.

2. Material and methods

2.1. Study sites: origin and selection

The study sites are part of the French RENECOFOR network (i.e. National Network for the long term Monitoring of Forest Ecosystems) managed by ONF (i.e. National Forest Board) (www.onf.fr/renecofor, last visited on 16-07-2018).

This network consists of 102 forest sites and is representative of a large variety of French forest species and geopedological groups (Brêthes and Ulrich, 1997). In order to benefit from available samples and data, the same 51 sites used in Redon et al. (2011) were monitored (Supporting Information (SI) Fig. S1). Certain sites are equipped with weather stations to sample rainfall (n = 27 sites), throughfall and soil solutions (n = 14 sites). These sites represent (i) nine forest species, (ii) four different climatic conditions (oceanic, transition, continental and mountainous), (iii) nine humus forms (subclass of mull, moder and mor) and (iv) seven soil types (SI Table S1). A wide dataset from these sites of mineral soils, humus and water physicochemical properties was collected by the RENECOFOR network (SI Table S2) (Brêthes and Ulrich, 1997; Ponette, 2010; Redon et al., 2011).

2.2. Sampling procedure, sample treatment and iodine analysis

Air-dried samples of litterfall, humus and mineral soil (0-40 cm) of forest soils were obtained from the RENECOFOR collection. Mineral soil (n = 50 sites) and humus (n = 51) were sampled between 1993 and 1995. In each site, this sampling was based on 25 points spatially distributed to represent the 0.5 ha area of the central part of the plot, and all the samples were oven-dried at 35 °C then stored in the dark at room temperature (for more details, see Jonard et al., 2017). Litterfall was collected in 0.5 m2 traps installed 1 m above the floor level and designed for a rapid drainage of precipitation to prevent sample decomposition. In each site, ten traps were systematically distributed in the 0.5 ha central part of the plot. Litterfall was harvested three to five times per year from 1995 to 2007, then dried, sorted and weighed. This study used litterfall samples pooled from early spring 1998 until late winter 1999 (after leaf fall in broadleaved forests), for 49 sites. Dried samples were crushed to obtain homogeneous powders. Composite samples were prepared mixing respective proportions of each fraction (i.e. leaves, branches, fruits and 'other' for litterfall; litter, fragmented and humic layers for humus; depth layers 0-10,10-20 and 20-40 cm for soil).

Rainfall, throughfall and soil solution at —20 cm were collected every week from September 2016 to August 2017, in a subset of sites (SI Fig. S1). Rainfall and throughfall were sampled with bulk collectors (including dry deposition), while the precipitation amount was measured in a separate reference rain gauge. Soil solution was sampled with suction cups. All samples were stored in the dark at 4 °C immediately after their collection. Analyses were performed every 28 days on composites made from four weekly samples pooled in proportion to their volume. The composites were filtered at 0.45 mm, but not acidified to prevent losses of I by volatilisation, and stored in the dark at 4 °C until analysis.

Alkaline extraction with tetra methyl ammonium hydroxide (TMAH) was used to extract total iodine from solid environmental samples as previously described (Roulier et al., 2018; Watts and Mitchell, 2008). Extraction was made in triplicate for each solid sample. Iodine concentrations were determined by inductively coupled plasma mass

spectrometry (ICP-MS) (Agilent 7500ce ICPMS, Agilent Technologies, Tokyo, Japan). Dissolved organic carbon was measured in soil solution with an elemental analyser (Shimadzu TOC-WVS).

2.3. Calculations

Element concentration values in rainfall, throughfall and soil solution are presented as weighted annual mean concentrations calculated from element concentrations and sample volumes (28- days composite samples) for one year period. Corresponding uncertainties were determined from analytical uncertainties based on relative standard deviation of ICP-MS replicate measurements of I intensities (10 replicates).

Iodine stocks in humus (g ha^{-1}) and litterfall iodine fluxes (g ha^{-1} yr^{-1}) were calculated by multiplying their iodine concentrations by the masses of these corresponding compartments (SI Table S2). Stocks of I in mineral soils were calculated by multiplying their iodine concentrations by the thickness (40 cm) and the bulk density of the soil layer (SI Table S2). Corresponding uncertainties were calculated from standard deviation of triplicate analyses of solid samples (extraction and ICP-MS analysis).

Iodine annual fluxes of rainfall and throughfall (g ha^{-1} yr^{-1}) were calculated as the sum of 28-days I concentrations in water multiplied by the corresponding 28-days hydrological fluxes (provided by ONF-RENECOFOR). Corresponding uncertainties were determined from the sum error propagation of concentration analytical uncertainties.

Where throughfall iodine fluxes were measured (n = 14), theoretical average residence times of I in humus and soil $_{(tresI)}$ were estimated using Equation (1). The calculation of $_{tresI}$ differed from Redon et al. (2011) to take into account total iodine inputs to soil (throughfall + litterfall) and not only rainfall iodine flux. It is assumed that (i) iodine distribution in studied ecosystems is in steady state and (ii) iodine input in the system from weathering bedrock to soil is negligible (Christiansen et al., 1989; Fuge and Johnson, 1986; Johnson, 2003).

$$t_{resI} = \frac{\text{stocks of I in humus} + \text{mineral soil}}{\text{total I input to soil}} \text{ (years)} \qquad (1)$$

where 'total I input to soil' corresponds to the sum of annual I fluxes through litterfall and throughfall (g ha^{-1} yr^{-1}).

In order to estimate iodine accumulation due to degradation of plant litter (from litterfall to humus), net I accumulation rates in humus were estimated using Equation (2) (Redon et al., 2011) with assumption that iodine input through rainfall/throughfall is not accumulated in humus:

$$\text{I accumulation rate} = \frac{([I]_{humus} - [I]_{litterfall}) \times DM_{humus}}{t_{resDM}} \ (g \ ha^{-1} \ yr^{-1}) \qquad (2)$$

where $[I]_{humus}$ and $[I]_{litterfall}$ are I concentrations in humus and litterfall (mg kg^{-1}), DM_{humus} is the humus dry mass (kg ha^{-1}) and tresDM is the average dry mass residence time in the humus layer calculated as (Equation (3); Redon et al., 2011):

$$t_{resDM} = \frac{DM_{humus}}{LF \times (1 - \text{litter fraction mineralized})} \ (\text{years}) \qquad (3)$$

where LF is the annual litterfall dry mass (kg ha^{-1} yr^{-1}) and 'litter fraction mineralized' is the average mass loss of litter due to mineralization during its transformation in humus. We used values previously selected by Redon et al. (2011) based on the dominating tree species studied from Osono and Takeda (2005): 85% in Pines, 70% in Douglas fir, 61% in Spruce, 51% in Silver fir, 65% in Beech and 43% in Oak forests.

Where iodine and carbon concentrations in soil solutions were known (n = 14), the iodine and organic carbon in situ concentration ratios ($C_R(I)$ and $C_R(C_{org})$, respectively) (L kg^{-1}) were estimated as the ratio of I or C_{org} concentrations in mineral soil (0-40 cm) (µg kg^{-1}) and annual weighted average I or C_{org} concentrations in the corresponding soil solution (at —20 cm) (µg L^{-1}) (Equation (4)). In the following, the iodine concentration ratio $C_R(I)$ is assimilated to in situ $K_D(I)$ based on the equilibrium hypothesis.

$$C_R(I \text{ or } C_{org}) = \frac{I \text{ or } Corg \text{ concentrations in mineral soil}}{I \text{ or } Corg \text{ concentrations in soil solution}} \ (L \ kg^{-1}) \qquad (4)$$

2.4. Statistical analyses

Statistical analyses were performed separately on iodine concentrations in litterfall, humus and soil compartments (denoted as response variables) in order to (1) search explanatory variables (listed in SI Table S3) that could potentially

influence them and (2) determine their correlation with the response variables. The following method was repeated for each compartment:

(1) Selection of explanatory variables: (i) by preselecting the explanatory variables correlated to response variables using univariate linear regression (ULR) ($p < 0.5$) and then (ii) by studying the correlation between these preselected explanatory variables to obtain a list of independent candidate explanatory variables to limit multicollinearity problems. These correlations were estimated by: the Pearson correlation matrix for numerical variables ($|r^2| > 0.7$), the Khi^2 test for categorical variables ($p < 0.05$) and an ANOVA test (analysis of variance) for numerical and categorical variables ($p < 0.05$).

(2) All the selected explanatory variables were considered in a multiple linear regression (MLR) model. The non-multicollinearity of the explanatory variables was checked with the variance inflation factor (VIF < 5). Fisher's test was performed to determine the significance of each explanatory variable.

Moreover, these linear regression models require that explanatory and response variables follow a normal distribution. Thus the assumptions of normality of distribution and homogeneity of variances necessary for results validity were checked with Shapiro—Wilk and Breusch-Pagan tests, respectively.

Relationships were studied between (i) iodine accumulation rates and tree species, (ii) in situ $K_D(I)$ values and soil properties, (iii) humus iodine stocks and tree species as well as (iv) $_{tres}I$ and C, Al and Fe stocks in soils. Iodine-related variables were response variables and other variables were also explanatory variables. A univariate linear regression and an ANOVA were performed when explanatory variables were numerical and categorical, respectively. Normality hypothesis of residues was evaluated with a ShapiroWilk test and then homogeneity of variances was evaluated by a Breush-Pagan test for the univariate linear regression and a Levene test for the ANOVA. When one of these hypotheses was not validated, a Spearman correlation for numerical variables and a Kruskal-Wallis test for categorical variables were performed.

Boxplots were used to represent the distribution of iodine concentrations and stocks, and iodine accumulation rates according to environmental conditions.

Statistical analyses and boxplot representations were performed using R Studio (R Core Team, 2013; version 3.4.3).

3. Results & discussion

Detailed iodine data for each site is available in SI Table S4. Iodine concentrations in litterfalls, humus and soils are presented in Fig. 1, whereas iodine stocks in humus and soils and iodine fluxes through litterfalls, rainfalls and

throughfalls are reported in SI Fig. S2.

3.1. Iodine inputs to forest soil: atmospheric deposition vs. litterfall

Throughfall iodine fluxes varied from 7.8 to 37.6 g ha^{-1} yr^{-1} (SI Fig. S2; mean = 17.8 g ha^{-1} yr^{-1}). On the whole, throughfall iodine fluxes were higher than corresponding rainfall iodine fluxes. This difference could be due to dry depositions as already observed (Roulier et al., 2018). Once iodine dry depositions leached by throughfall were taken into account, it appeared that iodine could be both absorbed and leached by leaves or needles.

Regarding litterfall, iodine concentrations varied between 0.25 and 2.56 mg kg^{-1} (Fig. 1) and the resulting iodine fluxes ranged from 0.7 to 8.2 g ha^{-1} yr^{-1} (SI Fig. S2). Statistical analysis showed that litterfall iodine concentrations were significantly positively correlated to rainfall I concentrations (Table 1 and Fig. 2, R^2 = 0.64), thus litterfalls under oceanic climatic conditions had higher I concentrations compared to other climatic conditions (SI Fig. S3; Kruskal-Wallis test, χ^2 = 19.49, p < 0.001). These results can be explained by the absorption of iodine from atmospheric de-positions of either leaves or needles, which returned to the forest floor after senescence. Bowley (2013) found also that vegetation I concentrations (mostly grass, clover, moss and heather) decreased with increased distance from the coast. Several authors have highlighted iodine absorption through leaves from rainfall and direct dry atmospheric deposition (Shaw et al., 2007; Tschiersch et al., 2009).

In conclusion, atmospheric I inputs were influenced by ocean/ sea proximity and were reflected in litterfall I concentrations through its absorption by leaves and needles. Considering the total I input to soil (i.e. throughfall + litterfall), inputs through litterfall contributed between 7 and 36% (mean = 17%), and atmospheric depositions (throughfall) were always the major I input to humus and soils (64-93%, mean = 83%).

3.2. Iodine concentrations and stocks in humus and mineral soils

Iodine concentrations in humus were, on average, 5 times higher than those in litterfalls (Fig. 1; 1.02-12.65 mg kg^{-1}, mean = 3.91 mg kg^{-1}). This average iodine concentration was lower than values reported by Bostock et al. (2003) in England (6-14 mg kg^{-1} for litter/humus layers) and Takeda et al. (2015) in Japan (11 mg kg^{-1} for litter/humus layers) for coniferous trees. Iodine stocks of humus varied widely from one site to another (SI Fig. S2; 4-873 g ha^{-1}) because of the large variability of humus mass (SI Table S2; 2-185 t ha^{-1}). Humus decomposition rate was slower under Pine, Spruce and Douglas fir forests (tresDM = 106 ± 103 years) compared to Oak, Beech and Silver-fir forests (tresDM = 9.1 ± 8.6 years), resulting in higher humus I stocks in the first forest group (median values = 271, 476 and 197 g ha^{-1},

respectively) compared to the second one (median values = 19, 18 and 58 g ha^{-1}, respectively) (SI Fig. S4; Kruskal-Wallis test, χ^2 = 20.74, p < 0.001).

Iodine concentrations in soils were, on average, higher than those in litterfall and humus, and showed a greater variability between sites (Fig. 1; 0.39-35.65 mg kg^{-1}, mean = 7.11 mg kg^{-1}). This average concentration was slightly higher than the average European concentration of 5.6 mg kg^{-1} (Johnson, 2003). Moreover, our concentration range was in line with that found for British soils (Johnson, 2003; Whitehead, 1984): 0.5-98.2 mg kg^{-1}. Iodine inventories in the studied sites highlighted the important stock of I in soils (SI Fig. S2; 2.2-69.4 kg ha^{-1}, mean = 21.9 kg ha^{-1}) compared to humus iodine stocks and litterfall iodine fluxes.

3.3. Humus: interface compartment between total I input to soil and mineral soil

Univariate linear regressions showed that humus iodine concentrations were significantly linked to: humus dry mass, dry mass residence time in the humus layer, soil I concentrations, tree species, humus forms and soil types (Table 1; p < 0.05). However, some of these explanatory variables are correlated with each other (SI Table S5; Pearson correlation matrix). Therefore, explanatory variables selected for the MLR model were t_{res}DM, humus C_{org} concentrations, soil and litter I concentrations. Multiple regression analysis showed that humus iodine concentrations were highly positively correlated with those in soil (Table 1; p < 0.001), suggesting that humus degradation could be a source of I for soil and/or that iodine concentrations in humus could partly result from upward transport by organisms from iodine-enriched mineral soil horizons (Fukuyama and Takenaka, 2004; Giesler et al., 2000; Kurihara et al., 2018). The dataset did not allow us to identify which of these processes were the most important. The second hypothesis was supported by the lack of correlation between humus I concentrations and those of litterfall on one hand, and total I input to soil on the other hand (Table 1; p > 0.05). It is likely that iodine in surface soil layers impacted humus I concentrations, at least partially, by masking a potential correlation with litterfall and atmospheric inputs. This was not observed previously by Redon et al. (2011) in these forest sites in the case of chlorine. These authors showed that the organic fraction of Cl in the humus layer was correlated with its carbon content and rainfall Cl inputs. However, the concentrations of Cl in mineral soils were significantly lower than those in humus (mean = 62 and 247 mg kg^{-1}, respectively), the opposite situation to iodine concentrations in our study (Fig. 1). Consequently, it seems possible that iodine enrichment in humus could also occur through litterfall and atmospheric deposit retention.

The calculated net I accumulation rates in humus, based on I concentration variations during the degradation of

litterfall to humus, ranged from 0.02 to 15.8 g ha^{-1} yr^{-1}, accounting for 0.1-82.3% of total I input to soil. On average, humus in Douglas fir, Oak, Silverfir and Spruce forests had a higher iodine accumulation rate (>4 g ha^{-1} yr^{-1}) than in Pine forests (<2 g ha^{-1} y^{-1}) (SI Fig. S5; Kruskal-Wallis test, χ^2 = 28.30, p < 0.001) despite its low organic matter turnover (tresDM = 144 ± 113 years). In the case of chlorine, Redon et al. (2011) determined negative Cl accumulation rates for Oak and Beech forests, due to Cl loss from the humus layer, but observed positive accumulation rates in Douglas fir, Silver fir, Spruce, and Pine forests. The net humus Cl accumulation mainly depended on the microbial transformation of Cl$^-$ to organic chlorine through organic matter decomposition (Montelius et al., 2015). For iodine, accumulation rates were always positive. Iodine enrichment in humus, compared to litterfall, is supposed to be linked to a process of adsorption as well as the possible iodination of organic matter, since soluble organic iodine is already the dominant fraction in throughfall (Gilfedder et al., 2008; Xu et al., 2016). Furthermore, humus I concentrations were positively linked to humus mass (Table 1; p < 0.001). Thus, easily degradable organic matter (mull), involving a lower humus mass, had on average a lower capacity of I retention than humus made of recalcitrant organic matter (moder) (SI Fig. S6; Kruskal-Wallis test, χ^2 = 6.19, p < 0.05) which leaded to iodine preservation in the humus.

In conclusion, although no correlation has been shown between total I input to soil and its concentration in humus, adsorption in this organic layer may provide an important temporary storage of iodine derived from atmospheric and biomass depositions. Apart from biomass, the role of potentially influential factors (e.g. microbial communities) or processes (e.g. bioturbation) remains unclear. Over the long term, humus forms the soil organic matter. This organic I reservoir can therefore subsequently be (i) a source of organically bound iodine refractory to turnover thus influencing the persistence of iodine in the soil or conversely (ii) a potential source of labile organic-iodine species which may be released to streams and groundwater. This last assumption is supported by the work of Xu et al. (2011a) that quantified ^{127}I and ^{129}I in humic and fulvic acids extracted from Savannah River soil. Their results indicated that fulvic acids, mobile organic matter, contained much higher iodine content (until around 20 times) than humic acids, less mobile.

3.4. Iodine in mineral soil: influence of soil properties and environmental conditions

Univariate regression analyses showed that $_{pHwater,}$ CEC, exchangeable Fe and Mn and litterfall I concentrations had no significant effects on iodine concentrations in mineral soils (Table 2; p > 0.05).

Conversely, soil iodine concentrations were significantly linked to: soil density, C_{org} and N concentrations, clay, silt and sand fractions, total Al, Fe and exchangeable Al concentrations, humus I concentrations, total I input to soil, tree species, climate conditions, humus forms and bedrock types. The Pearson correlation matrix showed that some of these explanatory variables were correlated (SI Table S6). Total organic carbon, nitrogen, iron (Fe_{tot}) and aluminium (Al_{tot}) concentrations were correlated with each other ($R^2 > |0.75|$). Previous studies showed that iodine could be linked to these soil constituents (Shetaya et al., 2012; Whitehead, 1973, 1978). Therefore, only C_{org} concentration was selected for the MLR analysis as it was representative of the correlation between iodine and these soil constituents. Likewise, sand, silt and clay fractions were significantly correlated with each other ($R^2 > |0.80|$). As iodine association with clay has been previously shown (Assemi and Erten, 1994; Fuge and Johnson, 1986; Hong et al., 2012; Sheppard and Thibault, 1992), only clay fraction was selected for the MLR analysis. As 'environmental conditions' (categorical variables) were dependent on selected quantitative variables, they were all excluded from the multiple regression analyses. Thus, multiple regression analyses showed that soil C_{org} and humus I concentrations were strongly correlated with I concentrations in soils (Table 2; $p < 0.001$ and $p = 0.0113$, respectively). Higher iodine concentrations were therefore generally observed in soils with higher organic matter, total iron and aluminium concentrations, with these three soil constituents being correlated. Nevertheless this statistical analysis does not allow us to determine which of these soil constituents had the greatest impact on the iodine concentrations in soils. This result is not surprising since sorption of organic matter on metal oxides surfaces has already been reported in several studies (Filius et al., 2000; Illes and Tombacz, 2006). Iodine association with soil organic matter has been often reported (Dai et al., 2009; Takeda et al., 2018; Whitehead, 1973; Xu et al., 2012), with iodine being covalently bound to organic matter. Iodine retention by metal (Al, Fe) oxides and hydroxides has also previously been observed by other authors (Dai et al., 2004; Takeda et al., 2018; Whitehead, 1973, 1978). Anion sorption occurs when positive charges appear on these (hydr)oxides, and inorganic iodine species react more strongly with metal oxides at low pH due to reduced competition with hydroxide for positively charged sites. Whitehead (1978) demonstrated for 154 soils in England and Wales that I concentrations were correlated with oxalate-soluble aluminium, with the OM content (1.24-27.5%) having no dominant influence on I concentrations. Takeda et al. (2018) also used correlation analysis to investigate which soil properties influenced I distribution in volcanic ash soil profiles. These authors found that iodine concentrations were significantly correlated with Al-humus complex concentrations, rather than OM concentrations in soils. In the current study, soil iodine concentrations were also correlated with soil nitrogen concentrations, these latter being correlated to soil C_{org} concentrations. This result is consistent with the work of Xu et al. (2012) who found correlation between iodine concentration and N/C ratio of natural organic matter extracted from a soil. These authors suggested that iodine in soil is associated with groups of N-containing compounds. In our study, a

weak positive correlation, at the limit of significance, was found for clay fractions ($p = 0.0495$), in agreement with studies suggesting that organic matter could have a stronger influence than clays for iodine retention (Assemi and Erten, 1994; Fuge and Johnson, 1986; Hong et al., 2012; Sheppard and Thibault, 1992).

Thus, environmental conditions characterized by accumulation of organic matter and existence of metal (hydr)oxides in soils would promote iodine retention in this compartment. In fact, we found that these soil properties were significantly different according to tree species and climatic conditions, resulting in significantly different iodine concentrations (Table 2). Soils under Douglas fir forests presented higher organic carbon and aluminium concentrations (mean = 58.7 and 8.7 g kg^{-1}, respectively) than soils under Oak forests (mean = 12.9 and 1.4 g kg^{-1}, respectively) (Kruskal-Wallis test, $\chi^2 = 22.55$ and $p < 0.001$ for C_{org} concentrations, $\chi^2 = 19.36$ and $p < 0.01$ for Al ones), resulting in higher soil iodine concentrations in Douglas fir forests (mean = 19.9 mg kg^{-1}) than in Oak forests (mean = 2.9 mg kg^{-1}) (SI Fig. S7; Kruskal-Wallis test, $\chi^2 = 23.15$, $p < 0.001$). Moreover, mountain soils were associated with higher Corg, Al_{tot} and Fe_{tot} concentrations (mean = 38.2, 6.9 and 7.5 g kg^{-1} compared to the overall mean of 26.1, 3.9 and 4.3 g kg^{-1}, respectively; Kruskal-Wallis test, $\chi^2 = 10.95$ $p < 0.05$, $\chi^2 = 15.14$ $p < 0.01$ and $\chi^2 = 21.60$ $p < 0.001$, respectively), due to soils subject to mountainous climates containing more iodine than soils subject to oceanic, transition and continental climates (SI Fig. S8; Kruskal-Wallis test, $\chi^2 = 13.82$, $p < 0.01$).

Surprisingly, a direct influence of coastal proximity on soil iodine concentrations was not observed in this study (Table 2; $p > 0.05$). Indeed, the two sites located in the coastal zone (SI Tables S1 and S4; PM85 and PM17 at < 2 km from the Atlantic Ocean, rainfall I flux of 14.9 and 14.3 g ha yr^{-1}, respectively) had the lowest I soil concentrations (<0.80 mg kg^{-1}) associated with the lowest OM, Fe_{tot} and Al_{tot} concentrations in soil (<6 g kg^{-1}) and the highest pH (8.55 and 8.70, respectively). Whitehead (1973) and Bowley (2013) also found no influence of distance from the coast. Bowley (2013) observed high iodine concentrations (127 and 274 mg kg^{-1}) in some soils near the coast (<1 km), but also a much lower concentration (9.3 mg kg^{-1}) despite a similar distance. This author did not find relationship between iodine concentrations and organic carbon, Altot, Mntot and Fe_{tot} concentrations of these soils (mean = 4.7, 1.5, 0.1 and 7.3 g kg^{-1}, respectively). In the current study, soil I concentrations were positively correlated with total iodine input to soils (Table 2 and Fig. 3; Pearson's correlation, $\tau = 0.6044$, $p < 0.05$).

In fact, iodine concentrations in soils seem to depend on both the supply of iodine and the ability of the soil to retain iodine, as previously outlined by Fuge and Johnson (1986). Indeed, sites having relatively important I inputs (>14 g ha^{-1} yr^{-1}) and high OM, Fetot ^{and} Al_{tot} concentrations in soil (>20, 6 and 4 g kg^{-1}, respectively) corresponded to highest soil I concentrations (>16 mg kg^{-1}) (SI Tables S2 and S4; DOU71, EPC08, EPC63, HET30). On the other hand, for soils with

significant iodine inputs (> 14 g ha^{-1} yr^{-1}) and small OM (<13 g kg^{-1}) and $_{Fetot}$ and $_{Altot}$ concentrations (<2 g kg^{-1}), iodine concentrations were low (<3 mg kg^{-1}) (SP57, CHP40, PM17, PM85). These results confirm that organic matter and Fe and Al (hydr)oxides allowed retention of incoming iodine.

This assumption was reinforced by exploring the proportion of iodine in soil that can be transferred to the liquid phase (the in situ KD(I)). Average annual iodine concentrations in soil solutions were 0.11-8.36 μg L^{-1} (SI Table S4; n = 13) resulting in a wide range of in situ KD(I) values from 242 to 192 855 L kg^{-1} (about a factor 800). This large range of values involves a great variability of soil I retention between sites. The highest in situ KD(I) value was obtained for the EPC63 site for which the $_{Corg,}$ total Fe and Al concentrations (86, 20 and 40 g kg^{-1}, respectively) were the highest of the studied sites, whereas the CPS77 site showed the lowest in situ KD(I) value and low levels of these soil constituents (9, 0.64 and 0.58 g kg^{-1}, respectively) (Pearson test between I and Corg, Altot and Fetot concentrations, p < 0.01). Gil-García et al. (2009) reported a geometric mean for KD(I) of 32 L kg^{-1} for organic soils (range of 8-581 L kg^{-1}) based on literature datasets. Most of KD(I) values from the literature were obtained after soils spiking with inorganic iodine forms and short contact times, probably explaining the large differences in values presented here. Our in situ KD values could better represent environmentally relevant steady state taking into account kinetics of biological and chemical processes involved in soil iodine retention on a longer time scale. A strong positive cor-relation between log-transformed in situ KD(I) and in situ CR(Corg) (Fig. 4, R^2 = 0.87; Pearson test, τ = 0.94, p < 0.001) was found, suggesting that iodine-containing dissolved organic matter could act as a source of mobile iodine. The importance of dissolved organic matter in binding iodine has been previously reported (Unno et al., 2017; Xu et al., 2011b). Xu et al. (2011b) demonstrated that a small fraction of soil OM, which may be readily mobilized, could behave as a source of iodine released in colloidal organic forms. Thus, iodinated organo-colloid could be leached by rainfall and then migrate into streamwater or groundwater.

Iodine retention in soils (t$_{resI}$, Eq. (1)) depends on soil constituents, resulting in a large scale of residence times of I in humus and soils considering throughfall and litterfall as iodine inputs (SI Table S4; 419-1756 years, n = 13, mean value = 1145 years). When these residence times were estimated using only rainfall input as made by others authors (Bowley, 2013; Redon et al., 2011), the values obtained ranged from 826 to 4511 years (SI Table S4; n = 13, mean value = 2033 years) and were 1.3-2.6 times higher than t$_{res(I)}$ obtained when considering the total iodine inputs to soils (i.e. throughfall + litterfall). These timescales agree with Bowley (2013) who estimated I inputs residence times from rainfall of between 284 and 2350 years (n = 20, mean value = 1207 years) for pasture soils of 20 cm in depth. Our theoretical average resi-dence time of I in humus and soil takes into account inputs from litterfall and throughfall but does not consider bedrock alteration, suggesting a possible overestimation of this residence time. However, several authors have claimed that

bedrock weathering represents a much lower iodine input to the soils than atmospheric one (Christiansen et al., 1989; Fuge and Johnson, 1986; Johnson, 2003). Furthermore, in this study we only considered annual inputs to the forest soils and iodine output fluxes were not quantified. Recommended geometric mean of soil iodine volatilisation rate is 0.021 yr^{-1} (Sheppard et al., 2006), such a rate applied to total iodine stocks in soils would correspond to the removal of 46-1442 g ha^{-1} yr^{-1}. Average emission of CH3I of 5-32 g ha^{-1} yr^{-1} (4.5-28.6 g(I) ha^{-1} yr^{-1}) has been measured in two conifer forest floor sites in Ireland (Dimmer et al., 2001). These literature estimates are indicative of the potential reemission of significant fraction of atmospheric iodine input. However, from the limited number of soil emissions fluxes, this estimation is subject to high error degree. Losses of iodine by leaching are suggested to be higher compared to losses by volatilisation (Bowley, 2013; Bostock et al., 2003). For example Bostock et al. (2003) quantified 1-6.5% of spiked iodine from forest and grassland soils by leaching compared to < 0.01% by volatilisation. In our previous study, we quantified annual iodine drainage flux about three times higher than total input one (i.e. throughfall + litterfall) in a beech forest (Roulier et al., 2018). In the current study, it is clear that iodine is retained in soils; however, it appears that the non-inclusion of iodine outputs from ecosystem relative to possible biomass exportation, drainage and volatilisation processes would lead to incorrect estimations (overestimation) about residence time of I in soils. Iodine residence times in studied humus and soils depended on Corg, Fetot and $_{Altot}$ stocks in soils (Pearson test, $\tau= 0.73$ p < 0.01, $\tau= 0.59$ p < 0.05, $\tau= 0.73$ p < 0.01, respectively). Thus, it appears that these components are the main factors influencing the persistence of iodine in studied forest soils.

In conclusion, the fate of iodine in forest soils studied showed an important variability with soil, vegetation and climatic conditions. The persistence of iodine in soils was mainly due to both total iodine inputs (throughfall + litterfall) and soil organic matter, total iron and aluminium concentrations. In these ecosystems, organic matter has a major role, both because of its sorption capacity leading to significant persistence of iodine in humus and soil, or acting as a source by releasing iodinated organo-colloid under some environmental conditions to streamwater or groundwater.

map (Fig. S1).

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Figures
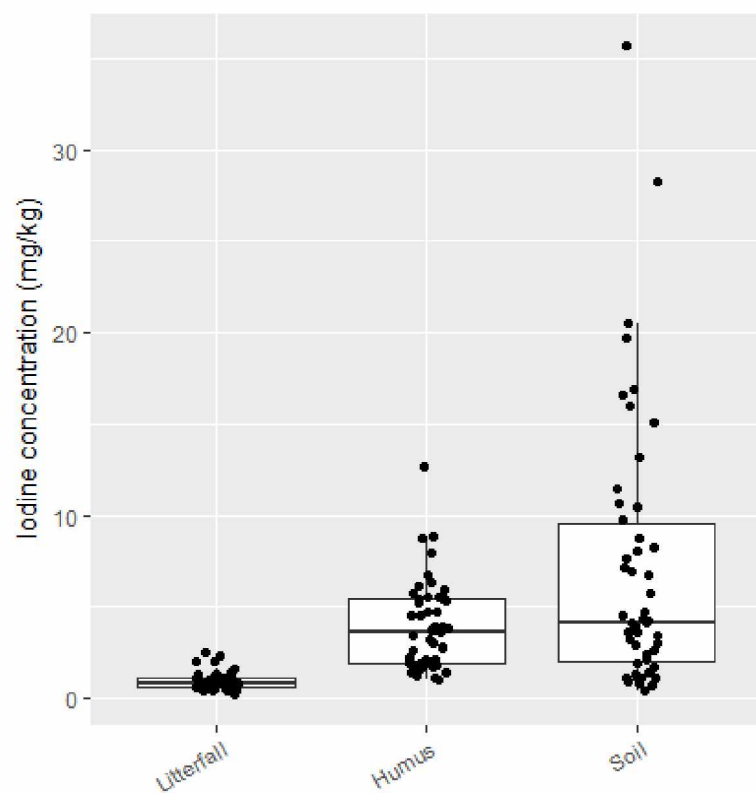
Figure 1 : Boxplots of iodine concentrations in litterfall (n = 49 sites), humus (n = 51 sites) and soil (n = 50 sites).
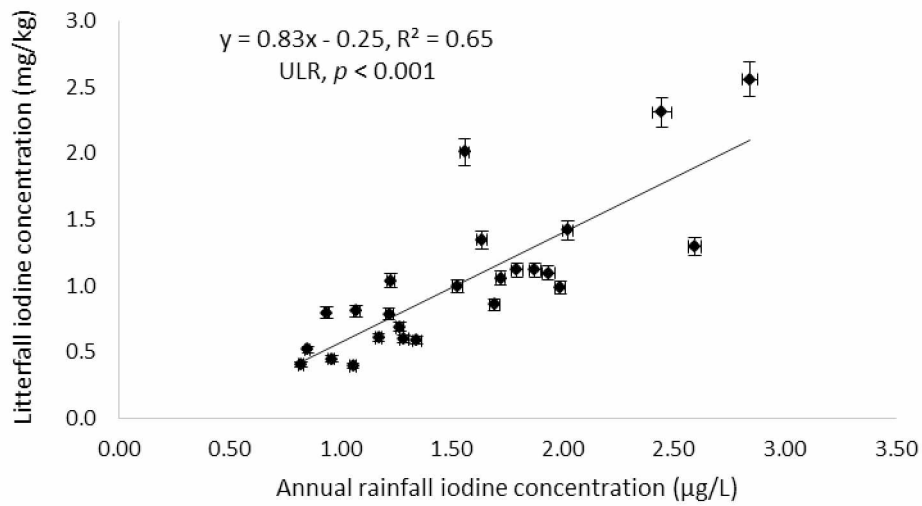
Fig. 2. Litterfall iodine concentrations as a function of weighted average annual iodine concentrations in rainfall (n =27 sites). Results correspond to n = 3 measurements for litterfall and n = 13 for rainfall.
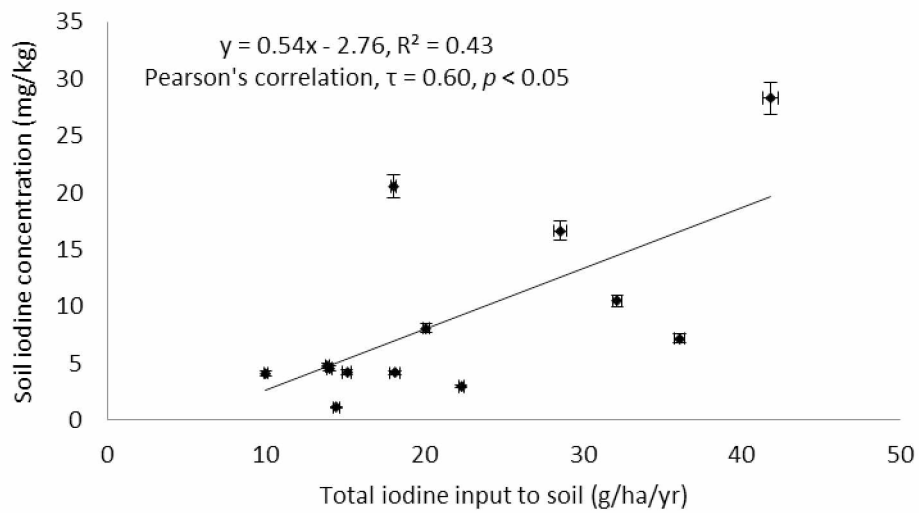
Fig. 3. Soil iodine concentrations as function of total iodine input to soil (i.e. throughfall + litterfall; n = 13 sites). Dots and error bars correspond to annual weighted average value and standard error, respectively.
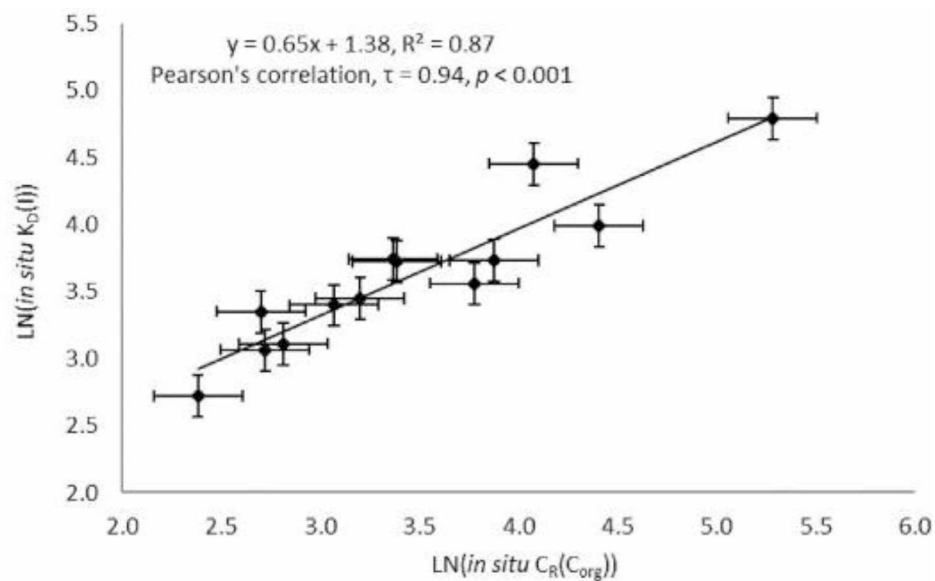
Fig. 4. Iodine in situ KD (Ln-transformed) as function of organic carbon in situ concentration ratio (Ln-transformed) (n = 14 sites). Dots and error bars correspond to mean value and standard error, respectively. Period: September 2016eAugust 2017 (n = 13 samples for each site).

Tables

Table 1 : Statistical analyses for litterfall and humus I concentrations. Summary of p-values obtained with the univariate linear regression (ULR) and the multiple linear regression (MLR) analyses. Non-significant variables are in black and significant variables are in blue.

Litterfall I concentrations (n = 49 sites)		
Candidate explanatory variables	ULR	MLR
Coastal distance	< 0.001 ***	-
Litterfall mass	0.0700	0.3194
Rainfall I conc.[1]	< 0.001 ***	0.0378 *
Throughfall I conc.[2]	0.2229	0.9699
Tree species (*n = 6*)	0.5287	-
Class of tree species[3] (*n = 2*)	0.9412	-
Climate conditions (*n = 4*)	< 0.001 ***	-
Humus I concentrations (n = 51 sites)		
Candidate explanatory variables	ULR	MLR
Coastal distance	0.8236	-
log10(Humus bmass)	< 0.001 ***	-
log10(t_{resDM})	< 0.001 ***	< 0.001 ***
Humus C_{org} conc.	0.3514	0.2442
log10(Soil I conc.)	< 0.001 ***	< 0.001 ***
Litterfall I conc.	0.1924	0.1093
Total I input to soil[4]	0.4444	-
Tree species (*n = 6*)	< 0.001 ***	-
Climate conditions (*n = 4*)	0.0962	-
Humus forms (*n = 9*)	< 0.001 ***	-
Soil type (*n = 7*)	0.0278 *	-

n = modality number; [1]for this explanatory variable, n = 27 sites; [2]for this explanatory variable, n = 14 sites; [3]class of tree species = deciduous or coniferous; [4]for this explanatory variable, n = 13 sites; *Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level; ***Correlation is significant at the 0.001 level; conc. = concentration

Table 2 : Statistical analyses for soil I concentrations. Summary of p-values obtained with univariate linear regression (ULR) and multiple linear regression (MLR) analyses. Nonsignificant variables are in black and significant variables are in blue.

Soil I concentrations (n = 50 sites)		
Candidate explanatory variables	ULR	MLR
Coastal distance	0.6545	-
Soil density	< 0.001 ***	-
pH_{water}	0.6379	-
Soil C_{org} conc.	< 0.001 ***	< 0.001 ***
log10(Soil N conc.)	< 0.001 ***	-
CEC	0.1980	0.2543
log10(Clay fraction)	0.0018 **	0.0495 *
Silt conc.	0.0426 *	-
Sand conc.	0.0439 *	-
Soil exchangeable Al conc.	0.0066 **	0.3441
Soil total Al conc.	< 0.001 ***	-
Soil exchangeable Fe conc.	0.1847	0.1450
Soil total Fe conc.	< 0.001 ***	-
Soil exchangeable Mn conc.	0.8627	-
Humus I conc.	< 0.001 ***	0.0113 *
Litterfall I conc.	0.6604	-
Total I input to soil [1]	0.0136 *	-
Tree species (*n = 6*)	< 0.001 ***	-
Climate condition (*n = 4*)	0.0100 **	-
Humus forms (*n = 9*)	0.0402 *	-
Soil types (*n = 7*)	0.1817	-
Bedrock types (*n = 3*)	0.0026 **	-

n = modality number; [1]for this explanatory variable, n = 13 sites;
*Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level; ***Correlation is significant at the 0.001 level; conc. = concentration
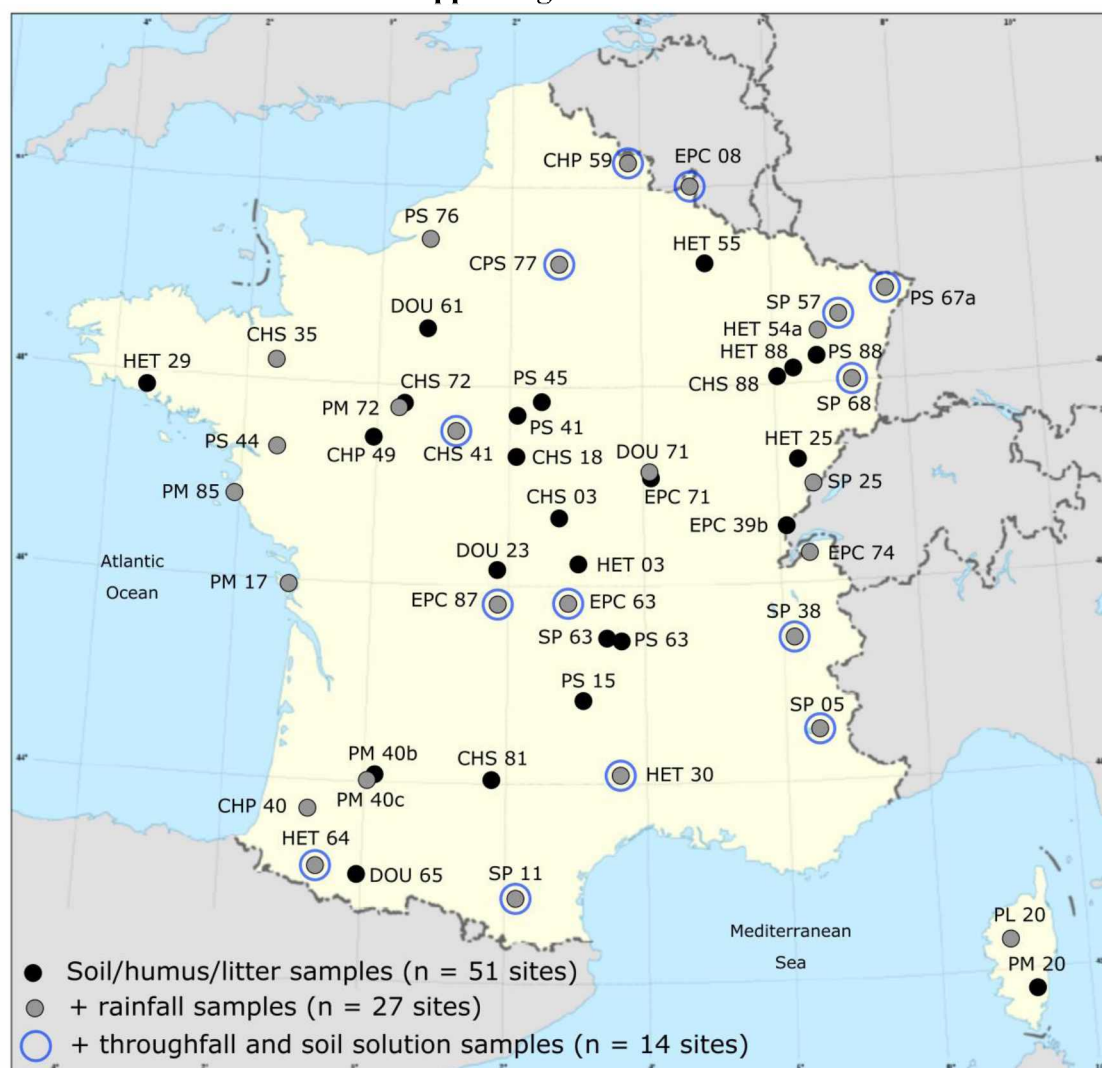
Figure S1. Studied forest sites and the corresponding compartments of the French RENECOFOR network. CHP=Pedunculate Oak; CHS=Sessile Oak; CPS=Sessile/Ped. Oak; DOU=Douglas fir; EPC=Spruce; HET=Beech; PL=Black Pine; PM=Maritime Pine; PS=Scots Pine; SP=Silver fir.
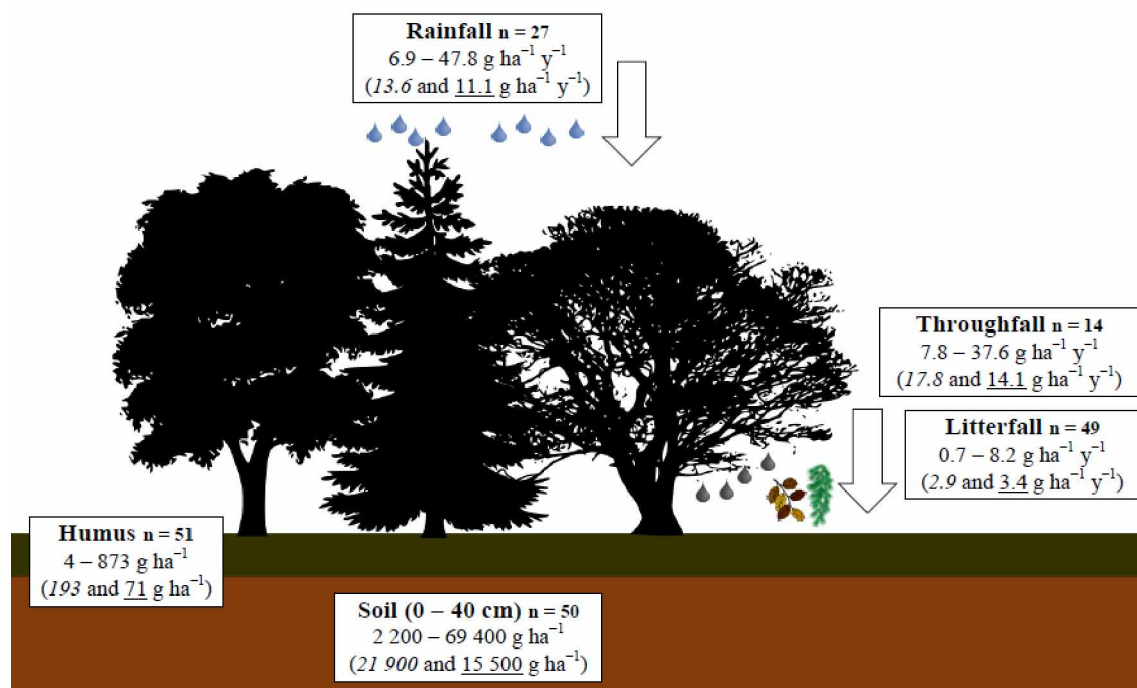
Figure S2. Iodine inventories in French forests. Range, *mean* and <u>median</u> values.
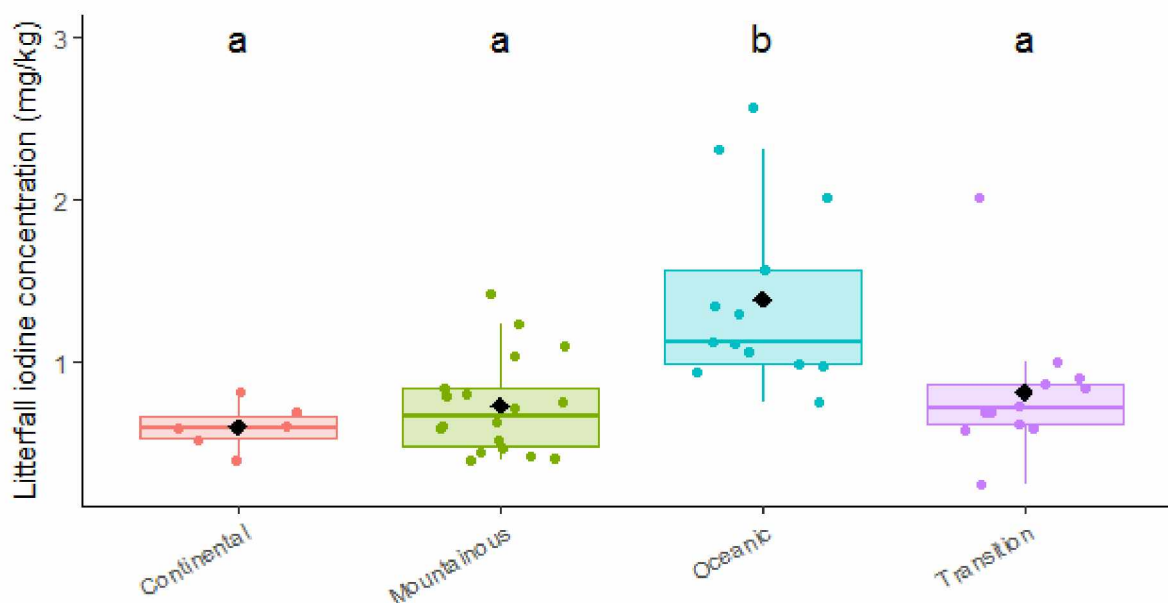
Figure S3. Boxplot distribution (distribution of data based on five number summary: minimum, first quartile, median, third quartile and maximum) of litterfall iodine concentrations against climatic conditions. The letters represent significantly different distributions according to pairwise Wilcoxon test, with Holm adjustment for *p*-values. Black dots correspond to mean value. Kruskal-Wallis rank for global test: $\chi^2 = 19.49$, *p*-value < 0.001.
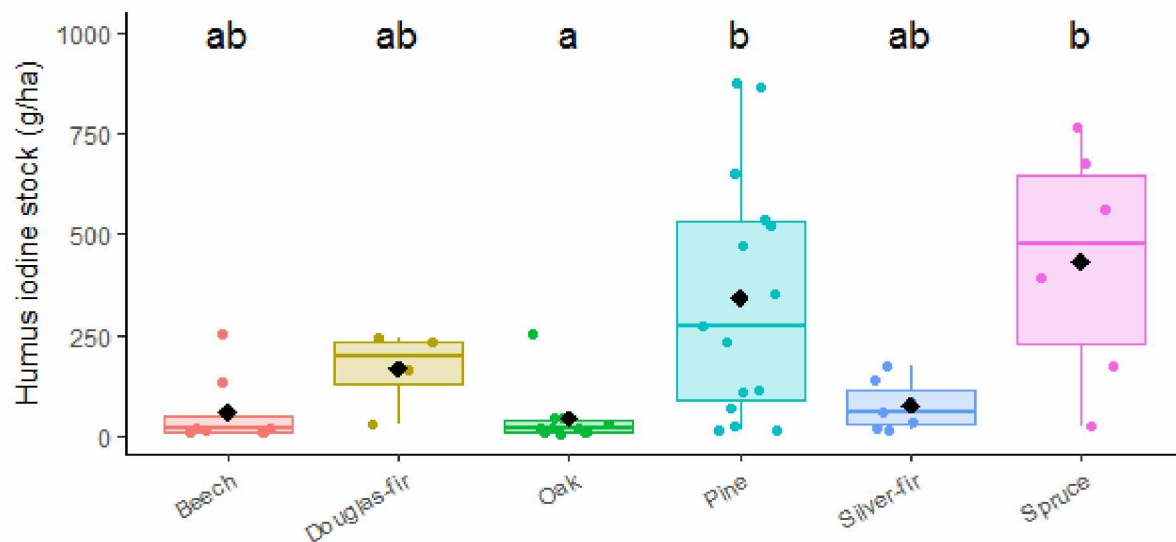
Figure S4. Boxplot distribution (distribution of data based on five number summary: minimum, first quartile, median, third quartile and maximum) of humus iodine stocks against tree species. The letters represent significantly different distributions according to pairwise Wilcoxon test, with Holm adjustment for *p*-values. Black dots correspond to mean value. Kruskal-Wallis rank for global test: $\chi^2 = 20.74$, *p*-value < 0.001.
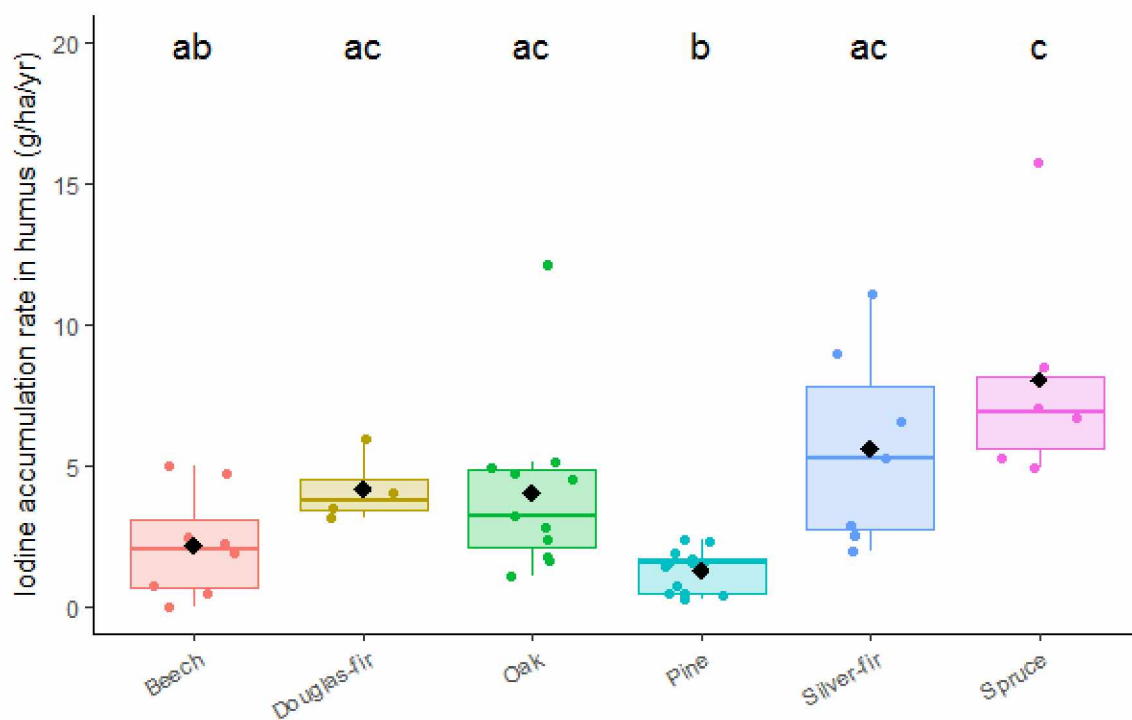
Figure S5. Boxplot distribution (distribution of data based on five number summary: minimum, first quartile, median, third quartile and maximum) of iodine accumulation rate in humus against tree species. The letters represent significantly different distributions according to pairwise Wilcoxon test, with Holm adjustment for *p*-values. Black dots correspond to mean value. Kruskal-Wallis rank for global test: $\chi^2 = 28.30$, *p*-value < 0.001.
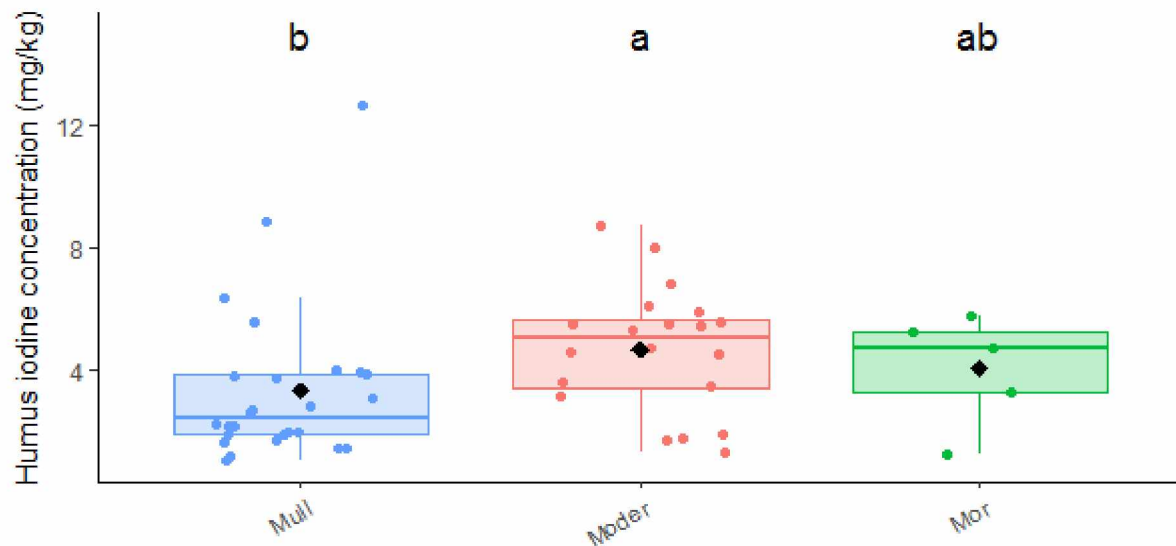
Figure S6. Boxplot distribution (distribution of data based on five number summary: minimum, first quartile, median, third quartile and maximum) of humus iodine concentrations against humus forms. The letters represent significant differently distributions according to pairwise Wilcoxon test, with Holm adjustment for p-values. Black dots correspond to mean value. Kruskal-Wallis rank for global test: $\chi^2 = 6.19$, p-value < 0.05.
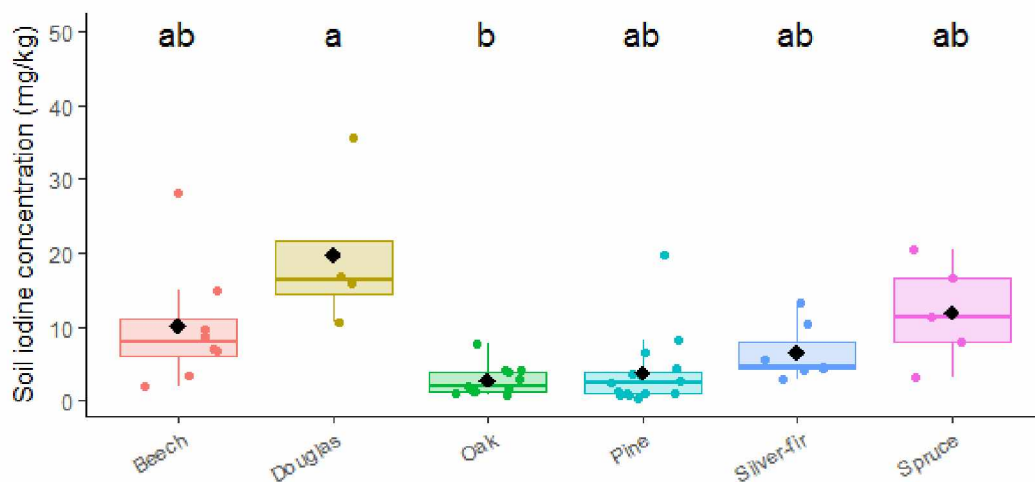
Figure S7. Boxplot distribution (distribution of data based on five number summary: minimum, first quartile, median, third quartile and maximum) of soil iodine concentrations against tree species. The letters represent significantly different distributions according to pairwise Wilcoxon test, with Holm adjustment for p-values. Black dots correspond to mean value. Kruskal-Wallis rank for global test: $\chi^2 = 23.15$, p-value < 0.001.
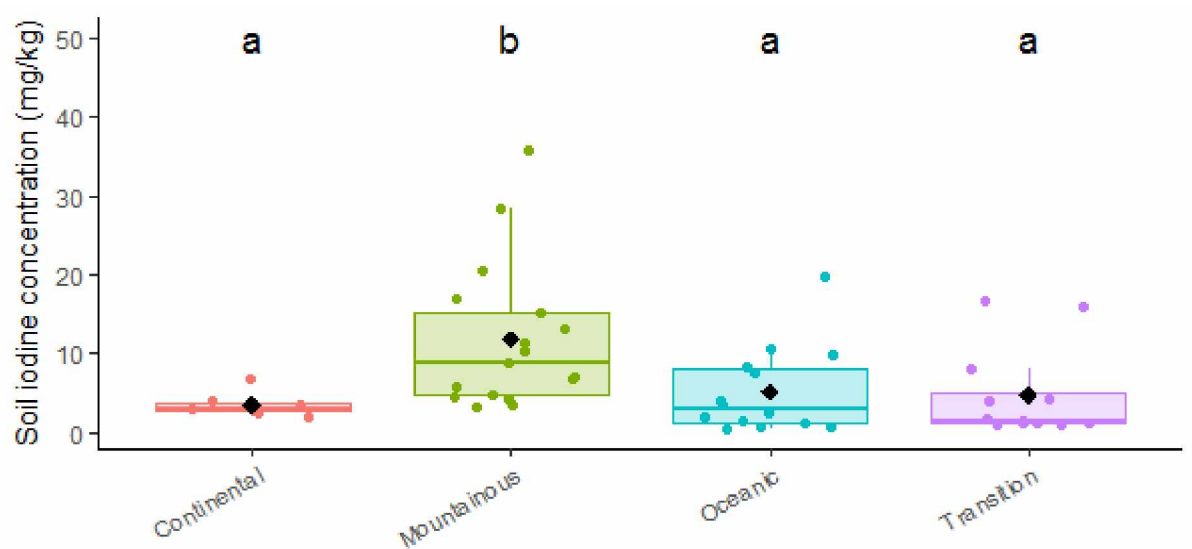
Figure S8. Boxplot distribution (distribution of data based on five number summary: minimum, first quartile, median, third quartile and maximum) of soil iodine concentrations against climatic conditions. The letters represent significantly different distributions according to pairwise Wilcoxon test, with Holm adjustment for p-values. Black dots correspond to mean value. Kruskal-Wallis rank for global test: $\chi^2 = 13.82$, p-value < 0.01.

Table S1. Environmental condition characteristics of studied sites.

| Forest site[1]	Dominant tree species[1]	Humus form[1,2]	Soil type[1,3]	Geological formation type	Climate[1]	Coast distance (km)[4]
CHP40	Pedunculate Oak	Eumull	Cambisol	Other	Oceanic	44
CHP49	Pedunculate Oak	Oligomull	Planosol	Other	Oceanic	161
CHP59	Pedunculate Oak	Mesomull	Podzoluvisol	Other	Oceanic	126
CHS03	Sessile Oak	Mesomull	Cambisol	Sedimentary rock	Transition	330
CHS18	Sessile Oak	Oligomull	Luvisol	Other	Transition	283
CHS35	Sessile Oak	Dysmoder	Luvisol	Igneous rock	Oceanic	47
CHS41	Sessile Oak	Moder	Luvisol	Other	Transition	220
CHS72	Sessile Oak	Moder	Planosol	Other	Oceanic	180
CHS81	Sessile Oak	Oligomull	Luvisol	Sedimentary rock	Transition	140
CHS88	Sessile Oak	Eumull	Cambisol	Sedimentary rock	Continental	410
CPS77	Sessile/Ped. Oak	Moder	Podzol	Other	Transition	206
DOU23	Douglas fir	Hemimoder	Cambisol	Igneous rock	Transition	230
DOU61	Douglas fir	Moder	Luvisol	Sedimentary rock	Oceanic	80
DOU65	Douglas fir	Dysmull	Cambisol	Other	Mountainous	131
DOU71	Douglas fir	Dysmoder	Podzol	Igneous rock	Mountainous	393
EPC08	Spruce	Moder	Podzol	Igneous rock	Transition	204
EPC39b	Spruce	Dysmull	Leptosol	Sedimentary rock	Mountainous	308
EPC63	Spruce	Dysmull	Andosol	Igneous rock	Mountainous	253
EPC71	Spruce	Moder	Podzol	Igneous rock	Mountainous	390
EPC74	Spruce	Mesomull	Luvisol	Igneous rock	Mountainous	277
EPC87	Spruce	Hemimoder	Cambisol	Igneous rock	Transition	226
HET03	Beech	Oligomull	Cambisol	Other	Mountainous	308
HET25	Beech	Eumull	Cambisol	Sedimentary rock	Mountainous	365
HET29	Beech	Dysmoder	Luvisol	Igneous rock	Oceanic	12
HET30	Beech	Dysmoder	Podzol	Igneous rock	Mountainous	67
HET54a	Beech	Mesomull	Planosol	Other	Continental	410
HET55	Beech	Hemimoder	Podzol	Sedimentary rock	Continental	277
HET64	Beech	Oligomull	Cambisol	Sedimentary rock	Mountainous	80
HET88	Beech	Mésomull	Cambisol	Other	Continental	426
PL20	Black Pine	Mésomull	Cambisol	Igneous rock	Mountainous/Med.	10
PM17	Maritime Pine	Mor	Arenosol	Sedimentary rock	Oceanic	2
PM20	Maritime Pine	Amphimull	Cambisol	Igneous rock	Mediterranean	20
PM40b	Maritime Pine	Mor	Podzol	Other	Transition	111
PM40c	Maritime Pine	Moder	Podzol	Other	Transition	97
PM72	Maritime Pine	Dysmoder	Planosol	Other	Oceanic	176
PM85	Maritime Pine	Moder	Arenosol	Sedimentary rock	Oceanic	1
PS15	Scots Pine	Moder	Cambisol	Igneous rock	Mountainous	165
PS41	Scots Pine	Mor	Podzol	Other	Transition	243
PS44	Scots Pine	Mor	Luvisol	Other	Oceanic	43
PS45	Scots Pine	Mor	Planosol	Other	Transition	244
PS63	Scots Pine	Dysmull	Cambisol	Igneous rock	Mountainous	210
PS67a	Scots Pine	Moder	Podzol	Other	Continental	427
PS76	Scots Pine	Mor	Podzol	Other	Oceanic	42
PS88	Scots Pine	Dysmoder	Podzol	Sedimentary rock	Mountainous	440
SP05	Silver fir	Oligomull	Cambisol	Other	Mountainous	113
SP11	Silver fir	Mesomull	Luvisol	Other	Mountainous	80
SP25	Silver fir	Mesomull	Leptosol	Sedimentary rock	Mountainous	348
SP38	Silver fir	Amphimull	Cambisol	Other	Mountainous	216
SP57	Silver fir	Oligomull	Cambisol	Sedimentary rock	Continental	417
SP63	Silver fir	Moder	Cambisol	Igneous rock	Mountainous	218
SP68	Silver fir	Mesomull	Cambisol	Other	Continental	409

[1]From Redon et al. 2011; [2]Classification according to the Référence Pédologique (AFES, 2009); [3]Classification according to WRB/FAO; [4]Estimated from www.google.fr/maps

Table S2. Physicochemical properties of soils (0 – 40 cm) and humus, humus and litterfall masses and dry mass residence time in humus (t_{resDM}) in studied sites (data provided by ONF – RENECOFOR).

Forest site	Bulk density (g cm^{-3})	pH	CEC (cmol kg^{-1})	Soil C_{org} conc. (g kg^{-1})	Soil N conc. (g kg^{-1})	Clay fraction (%)	Silt fraction (%)	Sand fraction (%)	Soil total Al conc. (g kg^{-1}) [1]	Soil exchang. Al conc. (cmol kg^{-1}) [1]	Soil total Fe conc. (g kg^{-1}) [1]	Soil exchang. Fe conc. (cmol kg^{-1}) [1]	Soil exchang. Mn conc. (cmol kg^{-1}) [1]	Humus C_{org} conc. (g kg^{-1})	Humus mass (t ha^{-1})	Litter mass (t ha^{-1})	t_{resDM} (year)
CHP40	1.28	5.07	2.65	10.69	0.90	13	43	44	0.76	0.60	2.24	0.02	0.03	339	2.42	3.98	1.1
CHP49	1.57	4.77	1.17	5.30	0.43	3	8	89	0.34	0.59	0.86	0.01	0.09	434	25.43	4.87	9.2
CHP59	1.16	4.74	6.23	15.65	1.25	18	77	5	2.02	3.20	5.30	0.05	0.08	381	6.93	5.86	2.1
CHS03	1.17	4.49	1.37	12.13	0.58	10	17	73	1.03	0.95	0.92	0.01	0.11	331	9.98	4.81	3.6
CHS18	1.42	4.53	1.35	9.46	0.51	14	38	48	0.83	1.00	1.08	0.01	0.03	423	21.89	4.19	9.2
CHS35	1.09	4.44	2.50	15.65	0.93	16	53	31	1.43	2.72	3.48	0.12	0.03	409	45.67	4.77	16.8
CHS41	1.31	4.44	3.75	13.83	0.81	15	54	31	1.36	2.99	3.11	0.04	0.07	509	6.15	5.51	2.0
CHS72	1.30	4.60	2.50	11.76	0.52	12	66	22	1.10	2.54	2.78	0.09	0.09	427	6.81	4.18	2.9
CHS81	1.17	4.71	5.63	20.90	1.34	25	64	11	2.90	4.58	4.95	0.02	0.05	434	6.09	4.10	2.6
CHS88	1.06	4.86	4.36	17.36	1.09	41	52	7	2.69	3.49	3.55	0.01	0.06	390	3.94	5.26	1.3
CPS77	1.35	4.83	0.67	8.67	0.52	5	13	82	0.64	0.45	0.58	0.01	0.14	317	26.21	4.62	10.0
DOU23	0.57	4.51	3.57	60.40	4.63	19	23	58	8.26	3.22	5.40	0.03	0.02	326	24.00	3.38	23.7
DOU61	1.07	4.36	3.16	21.08	1.08	10	45	45	3.08	3.12	4.69	0.06	0.07	332	29.00	1.82	53.2
DOU65	0.49	4.44	4.54	68.02	5.00	16	28	56	11.24	3.77	8.69	0.02	0.06	491	4.96	2.65	6.2
DOU71	0.27	4.29	5.99	85.45	4.10	18	24	58	12.04	6.33	10.53	0.15	0.06	381	40.10	1.98	67.4
EPC08	0.76	4.30	4.00	28.22	2.10	29	62	9	4.81	3.49	6.43	0.13	0.04	461	64.39	3.24	50.9
EPC39b	-	-	-	-	-	-	-	-	-	-	-	-	-	460	60.52	1.12	138.1
EPC63	0.41	5.22	3.91	85.84	6.61	30	48	22	40.17	2.32	19.83	0.07	0.09	356	44.34	4.80	23.7
EPC71	0.59	4.52	3.78	40.14	1.72	14	23	63	5.89	4.27	5.00	0.12	0.02	356	122.67	3.60	87.3
EPC74	0.99	6.18	16.54	31.05	2.37	34	29	37	1.44	0.32	3.68	0.01	0.04	404	8.77	6.38	3.5
EPC87	0.69	4.57	4.06	40.22	2.59	18	14	68	5.38	5.06	4.22	0.11	0.00	400	32.29	3.84	21.5
HET03	0.85	4.32	3.67	14.69	1.04	24	30	46	3.46	3.48	5.41	0.01	0.25	446	16.15	3.61	12.6
HET25	1.00	6.19	17.52	26.96	2.37	35	64	1	5.10	0.15	5.52	0.00	0.04	412	4.73	4.32	3.1
HET29	0.92	4.51	3.65	26.76	1.34	18	45	37	3.03	2.58	4.15	0.07	0.01	464	24.39	4.10	16.8
HET30	0.45	4.58	5.73	67.49	3.17	25	27	48	7.09	4.88	14.27	0.13	0.05	347	42.99	2.98	40.8
HET54a	0.88	4.60	3.72	16.80	1.07	17	59	24	2.00	1.95	3.35	0.00	0.33	342	9.98	4.67	6.0
HET55	1.33	4.56	3.02	12.38	0.67	10	41	49	0.77	2.45	1.64	0.02	0.07	452	8.37	3.68	6.4
HET64	1.11	4.84	6.04	14.60	1.34	41	49	10	3.27	1.99	7.85	0.01	0.27	479	8.51	3.48	6.9
HET88	1.04	4.67	3.81	14.40	0.85	22	30	48	2.67	3.13	2.59	0.01	0.15	392	10.29	4.42	6.6

[1]measurement made on samples sampled in 2009; - : not measured; conc. = concentration; exchang. = exchangeable

Forest site	Bulk density (g cm⁻³)	pH_{water}	CEC (cmol kg⁻¹)	Soil C_{org} conc. (g kg⁻¹)	Soil N conc. (g kg⁻¹)	Clay fraction (%)	Silt fraction (%)	Sand fraction (%)	Soil total Al conc. (g kg⁻¹)[1]	Soil exchang. Al conc. (cmol kg⁻¹)[1]	Soil total Fe conc. (g kg⁻¹)[1]	Soil exchang. Fe conc. (cmol kg⁻¹)[1]	Soil exchang. Mn conc. (cmol kg⁻¹)[1]	Humus C_{org} conc. (g kg⁻¹)	Humus mass (t ha⁻¹)	Litter mass (t ha⁻¹)	t_{resDM} (year)
PL20	1.04	5.44	3.64	25.33	0.87	17	23	60	5.50	1.05	4.30	0.01	0.08	421	13.91	4.21	22.1
PM17	1.41	8.70	4.22	3.85	0.18	1	0	99	0.00	0.00	0.38	0.00	0.00	251	92.50	3.37	183.0
PM20	0.62	5.62	5.65	53.16	2.38	20	35	45	10.02	1.01	6.01	0.01	0.07	398	30.51	3.79	53.7
PM40b	1.30	4.13	3.31	31.13	0.85	1	2	97	0.15	0.87	0.19	0.05	0.00	484	9.96	4.97	13.3
PM40c	1.36	4.53	2.77	23.45	0.86	5	2	93	1.12	1.72	0.09	0.03	0.00	480	8.33	4.81	11.5
PM72	1.09	4.35	2.50	25.67	0.84	4	11	85	0.79	1.49	0.99	0.09	0.00	372	49.90	2.77	120.3
PM85	1.35	8.55	5.77	5.55	0.26	2	2	96	0.01	0.00	0.39	0.00	0.00	101	130.22	2.85	305.0
PS15	0.80	4.89	3.47	26.33	1.60	20	25	55	5.73	2.48	5.25	0.02	0.10	398	20.42	3.54	38.4
PS41	1.35	4.61	1.40	6.39	0.37	4	9	87	0.80	1.13	1.11	0.05	0.01	421	83.65	4.26	130.9
PS44	0.97	4.28	5.01	32.82	1.35	18	55	27	1.97	3.78	0.82	0.05	0.00	444	92.93	3.86	160.5
PS45	1.18	4.34	5.84	14.87	0.64	10	20	70	1.06	2.78	1.52	0.14	0.00	259	184.64	3.74	328.8
PS63	0.54	5.00	3.92	22.49	1.06	23	31	46	2.77	2.35	3.51	0.03	0.10	401	27.60	2.98	61.7
PS67a	1.24	4.27	2.48	19.42	0.92	7	3	90	1.89	2.08	1.30	0.09	0.01	381	143.02	4.77	199.7
PS76	0.90	4.20	1.87	11.94	0.39	7	24	69	1.10	1.51	2.09	0.16	0.02	348	166.60	3.33	333.3
PS88	1.02	4.43	2.28	13.60	0.52	12	12	76	3.44	2.28	3.67	0.11	0.00	382	95.69	3.18	200.3
SP05	0.88	6.18	20.31	29.58	2.51	46	47	7	1.87	0.03	4.19	0.00	0.06	337	28.08	4.37	13.2
SP11	1.27	7.24	25.22	22.69	1.94	45	53	2	2.90	0.07	7.06	0.01	0.08	474	5.04	2.08	5.0
SP25	0.93	5.76	19.76	31.09	2.50	50	48	2	4.16	0.52	9.69	0.00	0.21	347	10.42	4.44	4.8
SP38	0.58	4.37	5.87	29.49	1.68	18	35	47	3.35	3.69	7.97	0.06	0.12	290	47.38	4.16	23.4
SP57	1.11	4.50	2.15	12.72	0.61	6	9	85	1.29	1.67	1.26	0.04	0.16	401	13.20	2.19	12.4
SP63	0.66	4.23	6.03	39.91	2.12	36	27	37	4.01	5.25	5.75	0.11	0.08	398	30.77	5.06	12.5
SP68	0.70	4.80	4.09	27.92	1.68	15	49	36	3.87	2.15	4.22	0.02	0.06	419	7.39	3.29	4.6

[1]measurement made on samples sampled in 2009; - : not measured; conc. = concentration; exchang. = exchangeable

Table S3. Numerical and categorical candidate explanatory variables versus studied response variables.

Response variables	Litterfall I concentrations (n = 49 sites)	Humus I concentrations (n = 51 sites)	Soil I concentrations (n = 50 sites)
Numerical variables	Coast distance	Coast distance	Coast distance
	Litterfall mass	Humus mass	Soil density
	Rainfall I conc.	t_{resDM}^2	pH_{water}
	Throughfall I conc.	Humus C_{org} conc.	Soil C_{org} conc.
		Soil I conc.	Soil N conc.
		Litterfall I conc.	CEC
		Total I input to soil	Clay, Silt, Sand fraction
			Total Al and Fe conc.
			Exchangeable Al, Fe and Mn conc.
			Humus I conc.
			Litterfall I conc.
			Total I input to soil
Categorical variables	Tree species	Tree species	Tree species
	Class of tree species[1]	Climate conditions	Climate conditions
	Climate conditions	Humus forms	Humus forms
		Soil type	Soil type
			Bedrock type

conc. = concentration; [1]class of tree species = deciduous or coniferous; [2]dry mass residence time

Table S4. Dataset related to average annual iodine concentrations and fluxes in rainfall, throughfall and soil solution, iodine concentrations, stocks and fluxes in litterfalls, humus and soils, iodine accumulation rates in humus and residence time of I in humus and soil in the studied sites.

Forest site	Iodine conc. (μg L^{-1})			Iodine conc. (mg kg^{-1})			Iodine stock (g ha^{-1})		Iodine flux (g ha^{-1} yr^{-1})			I acc. rates (g ha^{-1} yr^{-1})	t_{resl} (year) (TF+LF)[1]	t_{resl} (year) (RF)[2]
	RF	TF	Soil solution	LF	Humus	Soil	Humus	Soil	RF	TF	LF			
CHP40	1.79	-	-	1.12	1.61	1.39	4	7109	18.86	-	4.46	1.11	-	-
CHP49	-	-	-	0.98	1.84	0.72	47	4527	-	-	4.77	2.38	-	-
CHP59	1.87	3.29	1.77	1.12	2.61	4.13	18	19122	9.11	11.57	6.56	4.97	1039	2073
CHS03	-	-	-	0.25	1.91	1.70	19	7971	-	-	1.20	4.54	-	-
CHS18	-	-	-	0.62	1.38	1.39	30	7869	-	-	2.60	1.81	-	-
CHS35	1.72	-	-	1.06	5.54	7.67	253	33444	11.07	-	5.05	12.15	-	-
CHS41	1.69	3.14	8.36	0.86	1.88	4.20	12	22050	9.21	10.38	4.74	3.20	1423	2501
CHS72	-	-	-	0.94	3.10	2.10	21	10954	-	-	3.93	5.14	-	-
CHS81	-	-	-	0.70	1.40	3.90	9	18274	-	-	2.87	1.63	-	-
CHS88	-	-	-	0.59	2.18	3.06	9	12925	-	-	3.10	4.76	-	-
CPS77	1.27	3.65	4.60	0.69	1.77	1.11	46	6005	6.85	11.27	3.19	2.84	419	826
DOU23	-	-	-	0.90	6.78	15.94	163	36356	-	-	3.04	5.96	-	-
DOU61	-	-	-	1.57	7.97	10.63	231	45547	-	-	2.85	3.49	-	-
DOU65	-	-	-	1.24	6.34	35.65	31	69389	-	-	3.28	4.05	-	-
DOU71	1.22	-	-	0.79	6.10	16.93	245	18572	13.95	-	1.57	3.16	-	-
EPC08	1.56	3.82	6.83	2.01	8.72	16.64	561	50419	11.30	22.04	6.52	8.48	1730	4511
EPC39b	-	-	-	0.60	12.65	-	766	-	-	-	0.67	5.28	-	-
EPC63	1.06	2.67	0.11	0.40	8.81	20.51	391	33226	9.36	16.14	1.92	15.76	1756	3592
EPC71	-	-	-	0.72	5.50	11.47	675	27124	-	-	2.59	6.71	-	-
EPC74	0.94	-	-	0.80	2.79	3.23	24	12791	9.24	-	5.11	4.95	-	-
EPC87	1.34	2.71	1.07	0.59	5.31	8.04	171	22319	15.55	17.85	2.27	7.08	1118	1344
HET03	-	-	-	0.63	1.02	8.74	16	29772	-	-	2.27	0.50	-	-
HET25	-	-	-	0.42	1.66	15.07	8	60104	-	-	1.81	1.90	-	-
HET29	-	-	-	2.01	5.44	9.79	133	36215	-	-	8.24	4.98	-	-
HET30	2.02	1.85	1.10	1.42	5.91	28.29	254	50356	47.83	37.61	4.23	4.74	1210	1058
HET54a	1.17	-	-	0.61	2.12	3.58	21	12602	8.42	-	2.85	2.50	-	-
HET55	-	-	-	0.69	1.27	1.92	11	10193	-	-	2.54	0.76	-	-
HET64	1.93	4.00	0.60	1.10	1.12	7.16	10	31719	24.51	32.26	3.83	0.02	879	1295
HET88	-	-	-	0.40	1.85	6.91	19	28607	-	-	1.77	2.27	-	-
PL20	2.59	-	-	1.30	1.93	8.24	27	34344	28.29	-	5.47	0.40	-	-
PM17	2.45	-	-	2.31	3.83	0.39	354	2204	14.34	-	7.78	0.77	-	-
PM20	-	-	-	0.76	3.77	19.75	115	48948	-	-	2.88	1.71	-	-
PM40b	-	-	-	0.85	1.24	1.12	12	5803	-	-	4.23	0.29	-	-
PM40c	1.53	-	-	1.00	1.67	0.88	14	4796	11.37	-	4.81	0.48	-	-
PM72	1.99	-	-	0.99	4.71	1.14	235	4970	10.94	-	2.74	1.54	-	-
PM85	2.84	-	-	2.56	3.61	0.80	470	4320	14.95	-	7.29	0.45	-	-
PS15	-	-	-	0.76	3.46	6.69	71	21306	-	-	2.69	1.44	-	-
PS41	-	-	-	0.73	3.24	1.34	271	7224	-	-	3.11	1.60	-	-
PS44	2.32	-	-	-	5.78	2.63	537	10152	13.41	-	-	-	-	-
PS45	-	-	-	0.60	4.69	1.13	866	5333	-	-	2.25	2.30	-	-
PS63	-	-	-	0.47	3.95	3.59	109	7691	-	-	1.40	1.56	-	-
PS67a	1.28	2.42	3.74	-	4.55	2.45	651	12177	6.95	7.85	-	-	-	-
PS76	1.63	-	-	1.35	5.24	3.46	873	12500	8.78	-	4.50	1.94	-	-
PS88	-	-	-	0.52	5.47	4.37	523	17843	-	-	1.66	2.36	-	-
SP05	1.28	2.30	2.84	0.60	3.07	4.52	86	15820	12.67	11.40	2.62	5.26	1135	1466
SP11	1.22	6.48	1.75	1.04	3.88	10.47	20	52987	10.88	30.00	2.16	2.87	1648	4254
SP25	0.82	-	-	0.41	5.53	13.21	58	49141	10.33	-	1.82	11.08	-	-
SP38	0.96	1.39	-	0.45	3.71	4.75	176	10957	11.55	12.02	1.87	6.60	802	964
SP57	1.07	4.18	5.54	0.81	2.69	2.93	36	12980	10.34	20.54	1.77	2.00	583	1163
SP63	-	-	-	0.85	4.51	5.74	139	15213	-	-	4.30	9.01	-	-
SP68	0.85	2.10	3.49	0.52	2.11	4.10	16	11435	7.52	8.28	1.71	2.55	1146	1383
Mean	*1.57*	*3.14*	*3.21*	*0.91*	*3.91*	*7.11*	*193*	*21874*	*13.6*	*17.8*	*3.41*	*3.74*	*1145*	*2033*
Median	*1.53*	*2.92*	*2.84*	*0.79*	*3.61*	*4.17*	*71*	*15517*	*11.1*	*14.1*	*2.87*	*2.55*	*1135*	*1383*
Min	*0.82*	*1.39*	*0.11*	*0.25*	*1.02*	*0.39*	*4*	*2204*	*6.9*	*7.8*	*0.67*	*0.02*	*419*	*826*
Max	*2.84*	*6.48*	*8.36*	*2.56*	*12.65*	*35.65*	*873*	*69389*	*47.8*	*37.6*	*8.24*	*15.76*	*1756*	*4511*

- : not measured; TF: Throughfall; LF: Litterfall; RF: Rainfall; [1]:t_{resl} calculated from TF and LF fluxes; [2]:t_{resl} calculated from RF flux; conc. = concentration; I acc. rates = I accumulation rates in humus

Table S5. Pearson correlation matrix of selected explanatory variables in order to explain humus I concentrations. Green color indicates significant variables.

	Humus C_{org} conc.	Humus N conc.	Litterfall I conc.	Humus mass	t_{res}DM	Soil I conc.
Humus C_{org} conc.	1					
Humus N conc.	0.38	1				
Litterfall I conc.	-0.23	-0.16	1			
Humus mass	-0.53	-0.13	0.29	1		
t_{res}DM	-0.48	-0.28	0.36	0.93	1	
Soil I conc.	0.23	0.46	-0.04	-0.05	-0.04	1

conc. = concentration

Table S6. Pearson correlation matrix of selected explanatory variables in order to explain soil I concentrations. Green color indicates significant variables.

	Soil density	CEC	Soil C_{org} conc.	Sand fraction	Exchang. Al conc.	Total Al conc.	Exchang. Fe conc.	Total Fe conc.	Humus I conc.	log10(Clay fraction)	Silt fraction	Soil N conc.
Soil density	1											
CEC	-0.09	1										
Soil C_{org} conc.	-0.82	0.15	1									
Sand fraction	0.26	-0.55	-0.16	1								
Exchang. Al conc.	-0.58	-0.29	0.49	-0.16	1							
Total Al conc.	-0.61	0.02	0.76	-0.21	0.24	1						
Exchang. Fe conc.	-0.33	-0.28	0.28	0.16	0.57	0.12	1					
Total Fe conc.	-0.71	0.29	0.77	-0.48	0.38	0.81	0.17	1				
Humus I conc.	-0.57	0.01	0.58	-0.06	0.38	0.51	0.59	0.50	1			
log10(Clay fraction)	-0.52	0.54	0.37	-0.86	0.32	0.32	-0.06	0.60	0.15	1		
Silt fraction	-0.34	0.28	0.18	-0.88	0.30	0.21	-0.01	0.44	0.09	0.81	1	
Soil N conc.	-0.80	0.39	0.90	-0.45	0.40	0.71	0.09	0.81	0.51	0.63	0.40	1

conc. = concentration; exchang. = exchangeable