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# Halogen Retention, Organohalogens, and the Role of Organic Matter Decomposition on Halogen Enrichment in Two Chilean Peat Bogs

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Natural formation of organohalogen compounds can be shown to occur in all natural environments. Peat bogs, which are built up exclusively of organic matter and cover approximately 3% of the total continental world area, are potentially significant reservoirs for organohalogen formation. Up to now, fluxes and retention rates of halogens and organohalogen formation in peat bogs were mostly unquantified. In our study, we investigated the retention of atmospheric derived halogens and the natural formation of organohalogens by differential halogen analysis in two peat bogs in southernmost Chile. Atmospheric wet deposition rates of chlorine, bromine, and iodine range between 600 and 36000, 6 and 160, and 1 and 3 mg m$^{-2}$ yr$^{-1}$, respectively. Mean annual net accumulation rates of these halogens in peat are calculated to be 12−72 mg of Cl m$^{-2}$, 1.7−12 mg of Br m$^{-2}$, and 0.4−1.2 mg of I m$^{-2}$. Retention rates are similarly high for iodine (36−46%) and bromine (7.5−50%), and substantially lower for chlorine (0.2−2%). To evaluate influences of peat decomposition processes on halogen enrichment, halogen concentrations were compared to carbon/nitrogen ratios (C/N). Our results indicate that up to 95% of chlorine, 91% of bromine, and 81% of iodine in peat exist in an organically bound form. The results also indicate that the concentrations of halogens, especially of bromine and iodine, in peat are largely determined by peat decomposition processes and that halogens are not conservative in bogs.

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## Introduction

The natural formation of organohalogen compounds is still subject to controversy despite the fact that the halogenation of hydrocarbons is well documented for nearly all natural environments. Gribble recently reported the occurrence of more than 3800 organohalogen compounds mainly containing chlorine, although some contained bromine and a few iodine (*1*); these organohalogens are produced by living organisms or during natural biogeochemical processes. The oceans are the single richest source of known biogenic organohalogens, which are biosynthesized by a vast array of marine organisms. Terrestrial plants, fungi, lichen, bacteria, some higher animals, and even humans are also known to account for the diverse collection of organohalogens. In the late 1970s, the group parameter of adsorbable organic halogens (AOXs) was developed by Kühn (*2*) to determine organic halogen pollution by anthropogenic sources, and this method was later used to investigate the natural formation of organohalogen compounds in soils, peats, and plants (*3*, *4*). Studies of samples of preindustrial origin have demonstrated that the widespread occurrence of organohalogens in soils and water is a result of natural halogenation of organic matter (*5*). Enzymatic processes such as those of haloperoxidases and halogenases are thought to be the major source of natural halogenated organic compounds in the environment (*6*, *7*). Chlorine can, for example, be bound to aromatic structures in humic substances by reactions involving enzymes such as chloroperoxidase (*8*), and binding of iodine to phenolic groups in humic substances has also been reported (*9*).

Most studies on the natural formation of organohalogens focus on the formation of organochlorine compounds in soils, since chlorine is the most abundant halogen in natural environments. An overview of the role of chlorine in natural systems is given by Winterton (*10*). The principle that soils act neither as a sink nor as a source of chloride is widely applied in biogeochemical modeling, and chloride in this context is referred to as a conservative element with respect to water. However, in a recent review published on the natural chlorine cycle (*11*), it is now thought that chlorine does not behave conservatively in soils; for example, chloride is involved in a multitude of processes that form volatile, semivolatile, and high-molecular-weight organic compounds. Even less is known about the fate of bromine and iodine in soils. One reason for this lack of knowledge is that, due to the complexity of soil systems, analytical procedures to measure different halogen species are either difficult or not yet available.

Studies on the dynamics of iodine and bromine indicate that both elements form stable organohalogen compounds in soils, through interaction with humic substances, which limits their availability for plant uptake (*12*−*14*). Although chlorine in plants mainly exists in the inorganic form, it can be transformed to organic forms during degradation of plant material (*15*, *16*). Myneni (*15*) shows that chlorine in living plants mainly exists as inorganic chlorine, but is transformed to aliphatic organochlorines and chlorinated phenols during scenscence and weathering of plant material. Aromatic organochlorine compounds were shown to be the most abundant forms of chlorine in humified plant material (*15*), and the amount of organically bound chlorine increases during the decomposition and humification of plant material, indicating that degradation and chlorination of organic matter are concurrent processes in soils (*8*, *15*). In contrast to chlorine, only very sparse information is available on the behavior of bromine and iodine in response to the degrada-

tion of plant material. Investigations thus far indicate that only a small proportion of the iodine and bromine in soils is available for plant uptake (*13*, *14*), and that there is an important relationship with organic matter. For example, several laboratory studies have confirmed that iodine is predominately bound to humic acids in seepage water from soils and in brown waters from peat bogs (*10*, *17*, *18*). Furthermore, the iodine bound to soluble humic substances undergoes microbial-induced changes, where iodine is bound to different molecular weight fractions of the organic matter during various stages of aging (*19*).

Rain-fed peat bogs, which receive all elements exclusively by atmospheric deposition, are widely used as environmental archives to reconstruct historical variations of element deposition or climate changes (*20*–*22*). Very limited research has been conducted on the historical distribution of halogens in peat (*5*, *23*–*26*). In some of these studies halogens are seen to be conservative, and therefore, changes in halogen concentrations in peat and pore water do predict changes in halogen concentrations in rainwater (*24*). Chagué-Goff and Fyfe, however, suggested that halogens in peat are associated with the organic fraction (*26*), and other studies have confirmed that halogens in peat predominately exist in the organic form as organohalogen compounds formed during peat evolution (*5*, *25*). Total organic halide (TOX) levels in peat show a wide range with values reaching up to 2000 mg kg$^{-1}$ in oceanic bogs (*5*). Formation of organohalogen compounds in peat bogs is also a source of halomethanes, which are compounds relevant for stratospheric ozone depletion. Moreover, the existence of high amounts of halogenated organic compounds in peat could explain the recently reported formation of dioxins and furans during peat burning (*27*). Up to now, little information was available about the retention of atmospherically derived halogens in bogs or the evolution of organohalogens in peat. In this study we have investigated two ombrotrophic peat bogs in the Magellanic Moorlands, Chile (S 53°) for retention of chlorine, bromine, and iodine. This is the first time the formation of organohalogen compounds of Cl, Br, and I during the decomposition of the organic matter has been examined in peat bogs.

## Materials and Methods

**Characteristics of the Bogs.** The peat cores were taken from two ombrotrophic bogs (GC1, SKY) located in different climatic zones of the Magellanic Moorlands, southernmost Chile (Figure 1); a detailed discussion of the ombrotrophic nature of the bogs is given elsewhere (*28*). The bogs have different trophic states in terms of the availability of plant nutrients as indicated by the different peat-forming plants. The GC1 bog (S 52°47.443′/W 72°56.616′) is a cushion plant bog, which is typical for the superhumid area. Cushion plants such as *Donatia fascicularis* and *Astelia pumilia* and some *Carex* species indicate a higher trophic level than for *Sphagnum* bogs, and *Sphagnum* mosses are mostly absent. The high supply of nutrients to this bog is attributed to the intense atmospheric deposition of sea-salt aerosols and the high precipitation rates in this area (>6000 mm yr$^{-1}$). SKY (S 52°30.668′/W 72°07.505′) is a raised bog located in the transition zone between the extremely humid zone of the Magellanic Moorlands and the dry grasslands, and is built up by cushion plants and *Sphagnum* moss. Due to the much lower precipitation rates at the SKY location (~1500 mm yr$^{-1}$), the supply of nutrients is much lower than at the GC1 location, which allows *Sphagnum* to grow. Both cores contain a tephra layer, which can be assigned to different eruptions of the Mt. Burney volcano (*29*).

**Sampling and Sample Preparation.** The cores were taken at the highest elevation of each bog, where hummocks, hollows, and trees were absent. The uppermost 2 m of the
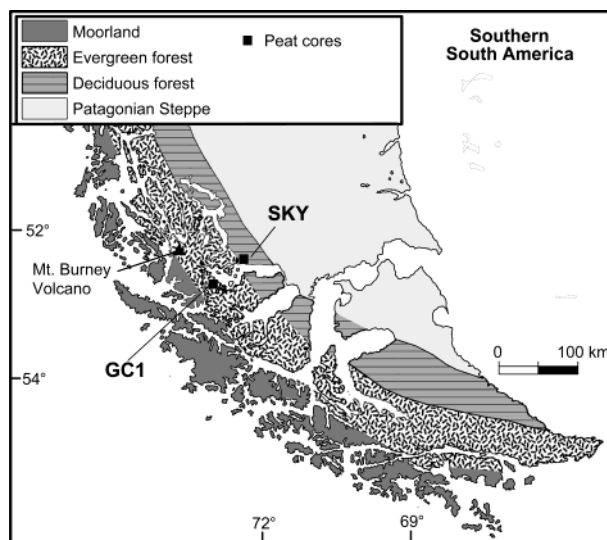


FIGURE 1. Map of southern South America and locations of the sampling sites GC1 and SKY.

peat was sampled using a $10 \times 10 \times 200$ cm stainless steel Wardenaar-type corer. Deeper sections were sampled with a stainless steel Russian-type barrel corer with a $50 \times 5$ cm cylindric sample chamber. All cores were sectioned in the field and placed into polyethylene bags. The GC1 core was sectioned into 2 cm slices, while the SKY core was sectioned into 4 cm slices. A layer of about 1 cm was cut off from each side of the core to avoid cross contamination due to smearing of material from the tephra layers. All samples were stored frozen. Half of each sample was freeze-dried and milled using a titanium centrifuge mill before analyses.

**Dating of Peat Samples.** The last 100 years could be dated using $^{210}$Pb techniques in the GC1 core only. A detailed description of dating techniques, used in this study, is reported elsewhere (*22*). All other ages were obtained by $^{14}$C dating. The activity of $^{14}$C was determined in humic acid extracts and in the humic acid extraction residues. Conventional $^{14}$C ages were calibrated using CALIB rev4.0, test version 6 (data set 1). All ages are given as means of 1$\sigma$ values.

**Differential Analysis of Halogens in Peat.** To distinguish inorganically and organically bound halogens in peat, inorganic halogens were removed prior to combustion by washing the sample with ultrapure water, acidified to pH 2 with concentrated nitric acid (*30*). Concentrations of chlorine, bromine, and iodine in untreated peat (total halogens, TCl, TBr, TI) and washed peat (OCl, OBr, OI) were determined after combustion of the peat samples (10–25 mg) and halogen trapping using an AOX analyzer (ECS 1000, Thermo Instruments GmbH, Germany). Halogens were then determined by means of ion chromatography, where chloride was detected through conductivity (Dionex, Germany), and bromide and iodide by UV/vis absorption (Shimazu, Japan). Halogen concentrations in the washed samples gave the amount of organically bound halogens. The differences in halogen concentrations between untreated and washed samples gave the amount of inorganic halogens. A detailed description of the method is given elsewhere (*30*).

**Sampling of Rainwater.** Rainwater was collected using a $50 \times 40$ cm polypropylene box connected to a 1 L Teflon bag. Collection was during the October 2002 and March 2003 campaigns; the period of collection was 2 days at location GC1 and approximately one week at the SKY location. Precipitation rates at the two locations were measured by an automatic weather station at each site over a period of one year (*31*).

**Determination of Halogens in Rain.** Total chloride in rainwater was determined by means of ion chromatography

TABLE 1. Halogen Concentrations in Rainwater (after a Wet and a Dry Period), Calculated Wet Atmospheric Halogen Deposition Rates, and Factors of Difference between Halogen Deposition Rates at the Bogs GC1 and SKY[a]

| | rain water ($\mu$g L$^{-1}$) | | | | deposition rate (mg m$^{-2}$ yr$^{-1}$) | | | |
| | GC1 | | SKY | | GC1 | | SKY | |
| | wet | dry | wet | dry | wet | dry | wet | dry |
|---|---|---|---|---|---|---|---|---|
| chlorine | 500 | 6000 | 400 | 2000 | 3000 | 36000 | 600 | 3000 |
| bromine | 3.9 | 26 | 3.8 | 7.8 | 23.4 | 156 | 5.7 | 11.7 |
| iodine | 0.48 | 0.44 | 0.68 | 0.55 | 2.6 | 2.6 | 1 | 0.83 |

[a] Calculations of atmospheric deposition of halogens are based on mean precipitation rates of 6000 mm yr$^{-1}$ at GC1 and 1500 mm yr$^{-1}$ at SKY.

and chloride detection through conductivity (Dionex, Germany). Total bromine and iodine in rain were analyzed by ICP-MS (Perkin-Elmer/Sciex Elan 6100 ICP-MS instrument) using [103]rhodium as an internal standard. Analysis of bromine and iodine species in rainwater was performed by IC−ICP-MS according to the method of Sacher et al. (*32*). Measurements of bromine and iodine were validated by comparison to a certified reference sample (CRM 611). All measurements of total bromine and iodine (indicative values) and bromide and iodide were in the range of the certified (indicative) values.

**Determination of Carbon and Nitrogen in Peat.** Carbon and nitrogen concentrations were determined by means of a C/N analyzer (ELEMENTAR) burning 10−20 mg sample aliquots in a tin capsule. Mean relative standard deviations (RSDs) for the determination of carbon and nitrogen were 2.2% and 2.1%, respectively ($n = 3$).

## Results and Discussion

**Atmospheric Deposition, Retention, and Net Accumulation of Halogens.** At both locations, the concentrations of all three halogens in rainwater were toward the bottom of the range usually observed at coastal sites. We assume that the comparatively low halogen concentrations in rain at both sampling areas are attributable to the generally high precipitation rates, especially at the GC1 location (>6000 mm yr$^{-1}$), which causes a continuous washout of sea-salt aerosols. Halogen concentrations in rainwater varied considerably, especially at the GC1 location, and were dependent on the predominant wind direction and precipitation rates. When eastern winds dominated and precipitation rates were generally low, the concentrations of all halogens were found to be comparatively high at both locations. Eastern winds coming from the Atlantic Ocean through the dry Pampa grasslands are assumed to carry high amounts of sea-salt aerosols. In times dominated by western winds, halogen concentrations in rain were generally lower since the high rainfall rates in the mountains (GC1 location) caused dilution of the sea salts in precipitation due to the strong washout. The high precipitation rates in the mountains do, therefore, cause a strong washout of sea-salt aerosols and explain why rainwater on the lee side of the mountains is relatively depleted in halogens. Due to the different climatic conditions at the two locations, halogen fluxes to the bogs differ to a large extent (Table 1). We assume that the rainwater concentrations at the bottom of the measured range are closer to mean annual values. The high values were found only during the first campaign after the weather had been dry for an 8 day period. After this dry period, the concentrations of chlorine and bromine in rainwater at GC1 were about a factor of 3 higher than in samples from SKY, whereas the values differ only slightly in samples taken during the wet period. The difference in concentrations and in annual precipitation rates between the two locations results in a difference in deposition rates of chlorine and bromine by a factor of 12 and 13, respectively, after the dry period, and only 5 and 4 in the wet period (Table 1).

In contrast to chlorine and bromine, iodine had similar values in samples of both campaigns, and concentrations were always higher in rain from the SKY location. Thus, the atmospheric iodine flux to GC1 is only higher by a factor of 2.6−3 than at SKY (Table 1). Whereas chloride and bromide in precipitation are derived mainly from sea spray, iodine in precipitation originates mainly from volatile organoiodine compounds (such as iodomethane) produced, e.g., by algae or microorganisms in the oceans or in the terrestrial environment (*12*, *33*−*36*). The lifetime of iodomethane is sufficient to allow long-distance transport in the atmosphere. The volatile organoiodine compounds are photolyzed in the troposphere, and the iodine oxides produced (*37*, *38*) are ultimately washed out by precipitation. Halogen speciation measurements in our rainwater samples show that a fraction of the total iodine at both locations exists as an unknown iodine species. At GC1 and SKY, 84% and 60% of the total iodine in rainwater, respectively, was iodide; the remainder was an unidentified, probably organic iodine species.

In this study we only considered the total wet deposition of halogens to calculate the annual input to the peat bogs. Dry deposition also contributes to the input of halogens to soils and peat, but it is difficult to measure, and is assumingly of lower importance due to the high precipitation rates in our chosen location. Therefore, we have not considered dry deposition during this study, and all calculations for deposition and retention of the halogens are based solely on rainwater data.

**Halogen Accumulation Rates in Peat.** The estimation of halogen retention in peat requires calculation of the net halogen accumulation rates in peat. In many bogs, organically bound elements, such as halogens or mercury, show a strong increase in net annual accumulation rates in the upper peat sections, as in our bogs (Table 2), which seem to indicate increased atmospheric deposition. However, increased accumulation rates can also be an effect of differences in mass accumulation caused by mass losses (carbon loss) during peat evolution (*28*). Due to the high loss of mass during peat decomposition, peat bogs must be considered as open systems, and thus, the true initial relationship between peat mass and element concentrations in the peat is unknown. The extent to which accumulation rates of an element in peat cores reflect true atmospheric deposition rates remains uncertain. To compensate for this effect of peat mass loss, we have suggested previously that element accumulation rates in peat be corrected for the differences in carbon accumulation rates between a highly humified reference section and less degraded sections in the upper parts of the bog; this normalization makes element accumulation rates calculated for peat layers with different degrees of decomposition comparable (*28*). The halogen accumulation rates given in Table 2 include both uncorrected values and values corrected for carbon accumulation. Mean annual halogen accumulation rates were calculated from the entire peat cores. The mass-loss-corrected mean halogen accumulation rates are only slightly different from the uncorrected values, since

TABLE 2. Average Concentrations and Uncorrected and Mass Loss Corrected Net Accumulation Rates of Cl, Br, and I in GC1 and SKY Peat Bogs[a]

| section (cm) | age[b] (yr) | C accum (g m$^{-2}$ yr$^{-1}$) | Cl concn (mg kg$^{-1}$) | Cl accum (mg m$^{-2}$ yr$^{-1}$) | Br concn (mg kg$^{-1}$) | Br accum (mg m$^{-2}$ yr$^{-1}$) | I concn (mg kg$^{-1}$) | I accum (mg m$^{-2}$ yr$^{-1}$) | MLCF |
|---|---|---|---|---|---|---|---|---|---|
| | | | | GC1 | | | | | |
| 0–18 | 110 | 64.6 | 1201 | 216/93 | 172 | 30.9/13.3 | 18.3 | 3.2/1.35 | 0.43 |
| 32–120 | 1910 | 27.5 | 1087 | 51.6 | 202 | 10 | 21 | 1.1 | ref |
| 0–120 | 2020 | | 1084 | 65.6/72.3 | 186 | 11.3/11.7 | 19.3 | 1.2 | |
| | | | | SKY | | | | | |
| 0–68 | 1090 | 23.3 | 349 | 18.1/11.8 | 56.3 | 2.92/1.89 | 10.1 | 0.53/0.34 | 0.65 |
| 68–120 | 760 | 27.5 | 418 | 24.8/13.6 | 60.2 | 3.57/1.96 | 14.4 | 0.86/0.47 | 0.55 |
| 120–244 | 4110 | 15.1 | 362 | 10.8 | 37.1 | 1.1 | 10.2 | 0.3 | ref |
| 0–244 | 5960 | | 366 | 14.7/12.1 | 47.9 | 1.93/1.65 | 10.9 | 0.44/0.37 | |

[a] Mass loss correction factors (MLCFs) were obtained by dividing the carbon accumulation rates in a reference section of highly decomposed peat by that in low degraded peat sections as proposed in ref 34. ref = highly decomposed reference peat section. [b] Calibrated radiocarbon years.

the reference section used for the correction of accumulation rates covers the largest part of the core (catotelm) and most of the mass loss effect is averaged out.

Even after correction for differences in mass accumulation, a slight increase in halogen accumulation in the upper peat sections could be observed in both bogs. Up to now, it was not clear to which extent this is due to an increase in halogen deposition or to halogen loss in deeper sections during peat aging. Studies on climate changes in southernmost South America do not indicate that variations in precipitation rates or an increase in wind speed promotes sea-salt aerosol formation, which could explain an increase in halogen deposition in the relevant period. The fact that the variations in halogen accumulation rates do not coincide in time at the two locations also argues against climatically induced changes in halogen deposition rates. Hence, we suggest that the changes in halogen accumulation in the two cores are mostly attributed to variations in peat degradation and/or dehalogenation processes.

**Halogen Retention Rates.** The differences in present atmospheric deposition rates measured at the two locations are not reflected by the net halogen accumulation rates estimated from the peat data. Mean net annual halogen accumulation rates at the two locations differ by a factor of 6 for chlorine and bromine and 3 for iodine (Table 2). Halogen retention rates, calculated from atmospheric wet deposition and accumulation rates at GC1 and SKY, are 0.2–2.4% for chlorine, 7.5–50% for bromine, and 36–46% for iodine (Table 2). Shotyk (24) reported values of bromine retention between 1.5% and 4.3% and 50–60 times lower values for chlorine retention in peat bogs of Scotland and the Shetland Islands. At the GC1 location the low retention found for chlorine relative to bromine and iodine is assumed to be mainly related to the higher runoff and the much higher atmospheric deposition rates of these halogens at this location. The reasons for the generally higher retention of bromine and especially iodine when compared to chlorine are not yet known. An important factor for the low chlorine retention is that concentrations of chlorine in rainwater are higher by 2–3 orders of magnitude than those of bromine or iodine (Table 1). It is therefore more probable that a higher percentage of iodine or bromine is sorbed and chemically bound to the organic matter than of chlorine. Moreover, physicochemical characteristics of the three halogens such as ionization energy and atomic radius would favor the formation of organo-bromine or organoiodine rather than the formation of organochlorine.

**Variations of Halogen Concentrations and Formation of Organohalogens.** Halogen concentrations in peat at both sites are comparable to those reported in other studies, reaching up to 2000 mg kg$^{-1}$ chlorine, several tens to hundreds of mg kg$^{-1}$ bromine, and several to tens of mg kg$^{-1}$ iodine

(23, 24, 26). Concentrations of chlorine and bromine are higher by a factor of 3 in GC1 peat, whereas iodine concentrations are only lower by less than a factor of 2 in SKY peat (Figure 2). The differences in halogen concentrations in peat between the two bogs are much lower than expected, on the basis of the large differences in atmospheric halogen deposition (Table 1). Mean concentrations of chlorine and bromine in GC1 peat are higher by a factor of ~3 than in SKY peat, whereas mean iodine concentrations differ only by a factor of ~1.7 as expected from the smaller differences in iodine wet deposition rates at the two locations (Table 2).

Results from halogen speciation measurements show that most of the halogenated compounds are organohalogens in both bogs (Figure 2). Organochlorine compounds comprise 82% of the total chlorine at GC1, and 93% at SKY, and 91–95% of all bromine was organically bound bromine (Figure 2A). A somewhat smaller fraction of the total iodine, 69% in GC1 peat (Figure 2A) and 81% in SKY peat (Figure 2B), is organoiodine. The reasons for the different behavior of iodine in peat are not yet known, although all three elements have been reported to form organohalogens easily in organic-rich soils (4, 13, 14). It is not certain if our data allow us to make conclusions about the stability of the formed organohalogen species. It is likely that, under these conditions, chlorine and bromine form more stable organohalogen compounds in peat and will not be as easily dehalogenated as iodine due to the higher bond strength of the C–Cl and C–Br bonds compared to that of the C–I bond. During reductive dehalogenation processes in the anaerobic peat sections, iodine could be reductively removed from the organic substrate and released into the pore water. Several biotic and abiotic processes of natural halogenation and dehalogenation in nature are known (39); however, there is still a lack of information on the dominant mechanisms that lead to the formation and destruction of organochlorine, -bromine, or -iodine compounds in extreme environments such as peat bogs.

In both peat cores, total bromine and iodine have their lowest concentrations in the uppermost peat section, followed below by a sharp increase within the upper 20 cm (Figure 2). In the GC1 core, iodine and bromine concentrations are highest between 10 and 50 cm and decline then by a factor of ~2 in deeper layers. In the SKY core, the increase in bromine and iodine concentrations is not as sharp as observed in the GC1 core. Here, the maximum is reached at a depth of ca. 65–70 cm followed by a continuous decrease down to the tephra layer at 180 cm. Both elements show a trend of slightly decreasing concentrations with depth in both cores. Organochlorine concentrations show a similar sharp increase in the uppermost peat layer in the GC1 core, but not in the SKY core, where total and organochlorine concentrations are high in the uppermost peat layer. One
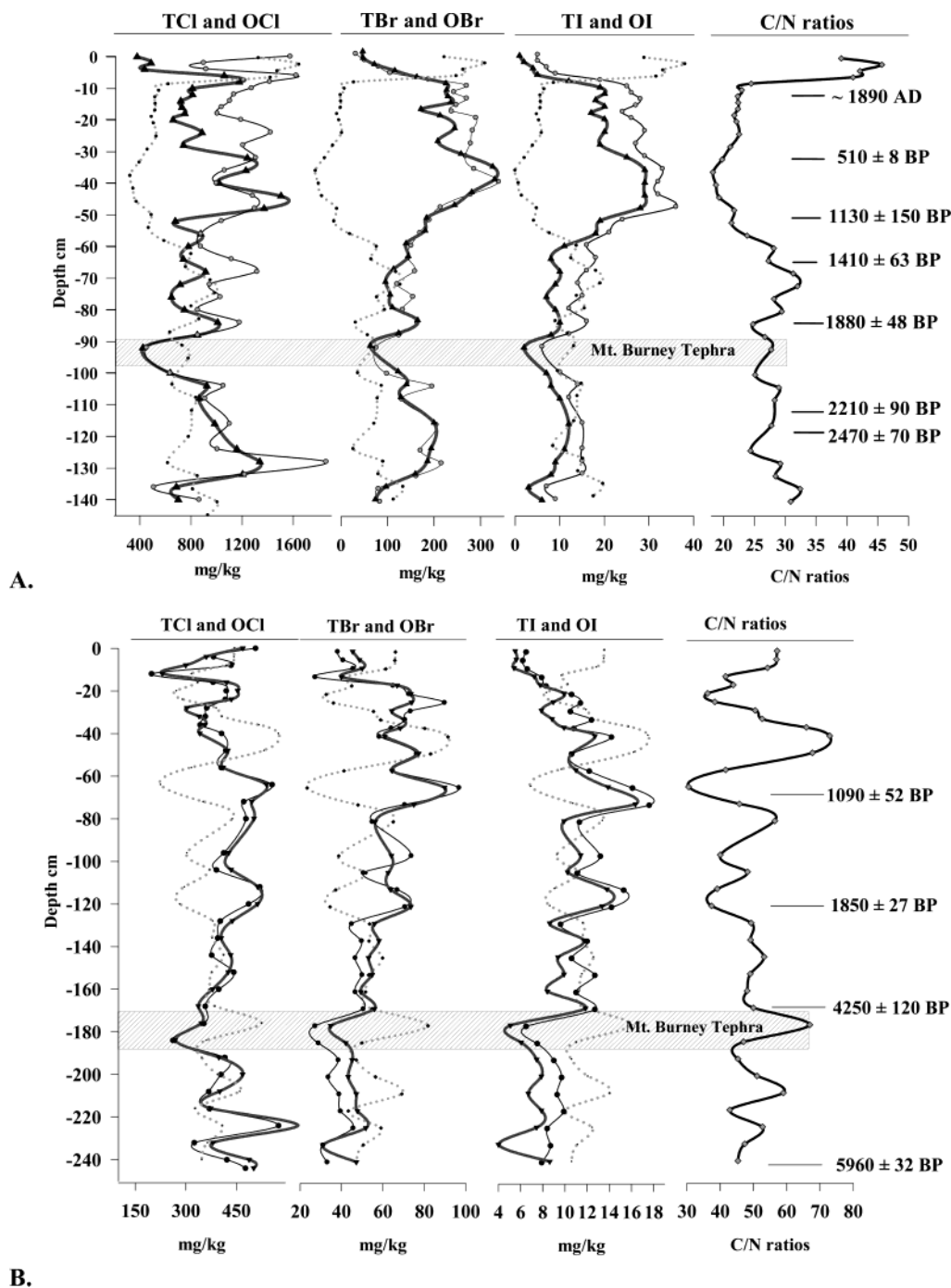
**FIGURE 2.** Chronologies of the GC1 and SKY peat cores, and concentrations of total (thin black line) and organically bound (thick gray line) chlorine, bromine, and iodine compared to C/N ratios in peat (gray spotted lines, and thick black line). Mean relative standard deviations (RSD) of TCl, OCl, TBr, Obr, TI, and OI are 8.7%, 11.7%, 7.1%, 8.2%, 5.9%, and 28.2% in GC1 peat (*n* = 3), respectively. In SKY peat RSDs for the same compounds are 9.6%, 9.2%, 3.7%, 11.1%, 7.3%, amd 9.3% (*n* = 3), respectively.

reason for this might be that the uptake of chloride by plants is significantly higher than that for bromide and iodide. Chlorine concentrations in plants can range between 700 and 21 000 mg kg$^{-1}$ dw (*40*), whereas average bromine and iodine contents are in the range of 1−5 and 0.1−0.4 mg kg$^{-1}$ dw, respectively. A recent study indicated that chlorine in plants does exist predominately in inorganic forms, but the chlorine is transformed into aliphatic and aromatic compounds during weathering of the plant material (*15*). It is therefore likely that, once the bog plants die, chloride is released and is only partly subject to formation of organochlorine compounds during humification of the plant material. In contrast, plant uptake of bromide and iodide is

much lower and there is a significant enrichment of bromine and iodine in soil as compared to plant material (*14*). Our data suggest that plant uptake is not relevant for the formation of organobromine and organoiodine compounds in peat. We assume that atmospherically derived bromine and iodine are predominately retained by humified plant material, and that formation of organobromine and organoiodine compounds is a result of direct sorption of the halogens to humic acids or is mediated by microbial activity (*18*).

**Concentrations of Organohalogens and Peat Decomposition.** Both cores show immense changes in halogen concentrations within the profile. A comparison of the organohalogen concentrations, which represent the largest
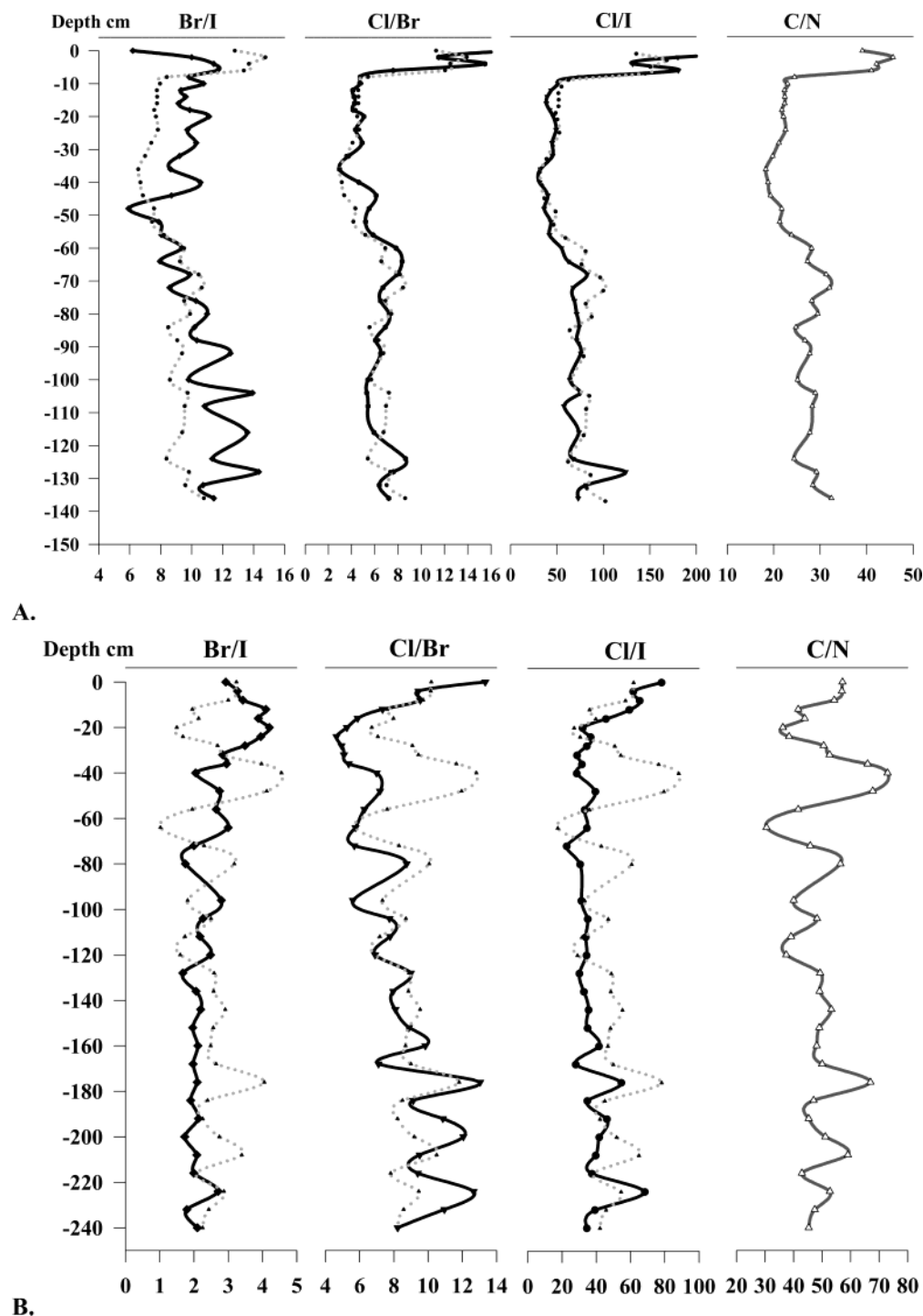
**FIGURE 3.** Relationship between peat decomposition expressed by C/N ratios (spotted lines) and ratios of organically bound halogens (Cl/I, Cl/Br, and Br/I) in the GC1 (A) and the SKY (B) cores.

portion of halogens in the peat, reveals that all three organohalogens have similar patterns of variation (Figure 2). To evaluate the relationship between enrichment of organically bound chlorine, bromine, and iodine in peat and peat decomposition processes, we determined carbon/nitrogen (C/N) ratios as a measure of changes in peat degradation. Decreasing C/N ratios indicate an increase in peat decomposition and vice versa. The decrease in C/N is thereby attributed to immobilization of nitrogen in the catotelm and preferential loss of carbon during peat decomposition in the catotelm (41). In Figure 2 we compare concentrations of organohalogens with C/N ratios in the two bogs. Previous studies have shown that total organohalogen

concentrations (TOX) in peat, which mainly reflect organochlorine compounds, depend mostly on the extent of peat degradation (5). Our results show that concentrations of organobromine and organoiodine compounds also increase with decreasing C/N ratios and vice versa. Therefore, we suggest that concentrations of all single organohalogen species, in both bogs, depend on the degree of peat decomposition. However, the functional relationship between C/N ratios and organohalogen concentrations in peat is not clear. One reason for that is that the chemical fate of organohalogens during peat degradation is poorly understood. Data of this study and also those of previous studies (28) indicate that this relation is not linear or exponential.

The increase in halogen concentrations as a function of peat alteration is most likely caused by an internal effect independent from climatically controlled variations of atmospheric halogen deposition. However, changes in the degree of peat decomposition are in many cases a signal of changes in the hydrological conditions in the bog. A drop of the water table as a result of decreasing precipitation rates will cause aeration of the upper parts of the bog, which will increase mineralization, humification, and mass loss. Accordingly, higher halogen concentrations in peat indicate drier rather than wetter conditions and higher halogen deposition rates. Climatic changes, concurrent with changes in the C/N ratios, have not yet been confirmed by other climatic proxies. The SKY bog is situated in a climatic transition zone and is subject to stronger variations of precipitation rates leading to intense fluctuations of the water table. This could explain the strong variations of C/N ratios especially in the upper sections of this core (Figure 2B). Such strong variations of the C/N ratios are not found in the GC1 peat, as climatic conditions are more stable in the superhumid zone. The reasons for the comparatively low C/N ratios in the 10–60 cm section of the GC1 core are not known (Figure 2A). As in the SKY core, the highest halogen concentrations are found in sections with lower C/N ratios. In the upper sections (acrotelm) of the GC1 core, the relationship between degradation of the plant material, as expressed by the C/N ratio, and formation of organohalogens is very pronounced. In the fresh plant material, where C/N ratios are higher, organohalogen concentrations are low, but they increase drastically when the organic material undergoes humification, which is accompanied by an intense loss of mass (80–90%) (*41*, *42*). We conclude that the enrichment of halogens during peat formation indicates that organohalogen formation and degradation of organic material are concurrent processes as was previously suggested for soils (*43*).

**Ratios of Organohalogens and Peat Decomposition.** Up to now, it was not known if organohalogen compounds are stable in peat or what happens to them during peat evolution. For aerated soils, the release of chloride during the mineralization of organochlorine-containing organic matter has been suggested (*4*). The comparison of halogen concentrations with C/N ratios in our peat profiles indicates that halogen concentrations do depend on peat decomposition. Apparently, diagenetically promoted enrichment of halogens in peat takes place in the upper peat sections as a result of water table fluctuations and aeration of previously water-saturated (anoxic) peat sections. Subsequent rising of the water table preserves the halogen concentration in a peat layer. However, it is not clear if all halogens are influenced by peat decomposition to the same extent.

To investigate differences in organohalogen enrichment during peat degradation, we compared organohalogen ratios of Cl/Br, Cl/I, and Br/I with C/N ratios (Figure 3). In this approach we assume that ratios of halogens in wet and dry deposition have been constant since the beginning of peat formation, and therefore, all observed changes in organohalogen ratios must be a result of peat alteration processes. If all halogens were equally affected by peat decomposition processes, then almost constant halogen ratios throughout the entire core would be expected. Figure 2 shows that Cl/Br ratios in both cores have a tendency to follow changes in C/N ratios, which means that the bromine concentrations in peat increase to a larger extent than chlorine concentrations when peat humification increases (lower C/N ratios). Cl/I ratios in the GC1 core also follow C/N ratios, indicating that iodine is enriched relative to chlorine (Figure 3A). This trend is weaker in the SKY core (Figure 3B), suggesting that iodine concentrations in the SKY bog are only slightly more affected by peat humification than chlorine concentrations. However, Cl/I ratios in the SKY core are generally lower than

in GC1 peat due to the relatively higher iodine concentrations in SKY peat. Br/I ratios run inversely to the C/N ratios in the SKY core, indicating that bromine is more enriched with increasing peat humification than iodine. The Br/I ratios in the GC1 core do not show a clear dependency on C/N ratios, which suggests that both halogens in this core are enriched to a similar extent during peat humification. However, the relationship between C/N ratios and halogen ratios as described here is solely based on the shape of the curves and gives only a trend with several exceptions throughout the profile. The observed relationships do not follow a linear function or any other known statistical correlation. This limitation is attributed to our poor understanding of the behavior of different organically bound elements during decomposition of organic matter, but will be subject to further investigations.

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