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Bromine and iodine in plant-soil systems

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Bromine and iodine in plant-soil systems

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Abstract

Bromine and iodine are known trace elements in the biosphere as a result of natural and anthropogenic processes (e.g. volatilization from sea, biomass burning). Though the fate of halogens in the environment has been studied intensely, a lack of knowledge still exists concerning their behaviour, distribution and speciation in terrestrial environments.

The aim of this work was to examine natural enrichment processes of halogens in terrestrial environments and to study the interactions between halogens, soil, litter and plants. Both terrestrial plants and soils may have an important influence on halogen cycles due to their capability of storing as well as emitting a wide range of halogen species.

Bromine and iodine fate were examined during annual ryegrass (*Lolium multiflorum)* life cycle (from seed to decomposition). In addition, Atlantic beech (*Fagus Sylvatica*) leaves were decomposed under laboratory condition in order to compare them to the natural decay processes. The bromine and iodine distribution were examined in soil, soil solutions, rocks, wet depositions, leaves and litter at two forest sites in the vicinity of Heidelberg, Germany. The halogens were measured using various methods such as INAA, XRF, ICP-MS and IC/ICP-MS.

During annual ryegrass decomposition the halogens release in both organic and inorganic species. Bromine mostly volatilizes (up to ~80%), while small amounts remain in the detritus (up to ~2.6%) and remaining bromine is leached. Iodine behaviour during decomposition is less conclusive and requires further investigations. Bromine release during Atlantic beech decomposition reveals a different pattern compared to annual ryegrass, reflecting the importance of litter quality on this process.

Bromine and iodine concentrations in the examined soil profiles range between 0.6-15 µg/g and in soil solutions they vary between 0.5-43 µg/l. A dependence to soil horizons is observed. In the topsoil (rich in organic matter), halogens tend to be in an organic form (between 60-100%), while in the lower soil sections the organic fractions decrease. The bromine and iodine source in one examined site is atmospheric deposition while in the other site an additional influence from basement rocks is observed.

The bromine volatilization from the decomposing Atlantic beech leaves (12.9% ± 6.1, experimental stage) was lower compared to the calculated loss in natural conditions (24.4%), indicating that litter can release bromine and act as a source.

This work shows that halogens are present in components of the terrestrial ecosystem, being exchanged between them and their presence and phase is influenced by biological processes (e.g. growth, decomposition).

Zusammenfassung

Brom und Jod kommen in von Folge sowohl natürlichen als auch anthropogenen Prozessen (z.B. Verdunstung von Meerwasser, Verbrennung von Biomasse) als Spurenelemente in der Biosphäre vor.

Obwohl das Verhalten von Halogenen in der Umwelt intensiv untersucht worden ist, bestehen nach wie vor große Lücken im Verständnis ihres Verhaltens, ihrer Verteilung und ihrer Bindungsformen in terrestrischen Milieu. Ziel dieser Arbeit war die Untersuchung natürlicher Anreicherungsprozesse von Halogenen in terrestrischen Milieu, sowie der Wechselbeziehungen zwischen Halogenen, Boden, Streu und Pflanzen. Sowohl terrestrische Pflanzen als auch Böden vermögen den natürlichen Halogen-Kreislauf entscheidend zu beeinflussen, indem sie sowohl als Speichermedium (Senke) als auch als Emittent (Quelle) einer vielzahl von Halogen-Spezies dienen.

Das Verhalten von Brom und Jod wurde während des einjährigen Lebenszyklus (vom Samen bis zur Zersetzung) von Weidelgras (*Lolium multiflorum*) untersucht. Darüber hinaus wurden Blätter von Buchen (*Fagus Sylvatica*) unter Laborbedingungen zersetzt, um diese Ergebnisse mit denen von Abbauprozessen unter natürlichen Umweltbedingungen zu vergleichen. Die Verteilung von Brom und Jod in Boden, Bodenlösung, Ausgangsgestein, Niederschlag, Blättern und Streu wurde in zwei Wald-Gebieten in der Umgebung von Heidelberg (Deutschland) untersucht. Zur Quantifizierung der Halogene kamen verschiedene Methoden zum Einsatz, unter ihnen INAA, XRF, ICP-MS und IC/ICP-MS.

Während der Weidelgras-Zersetzung werden die beiden Halogene sowohl in organischer, als auch anorganischer Form freigesetzt Brom in überwiegend flüchtiger Form (bis zu ~80%), während kleine Mengen im Detritus verbleiben (bis zu ~2,6%) und die restliche Menge ausgewaschen wird. Das Verhalten von Jod während der Zersetzung ist weniger schlüssig und bedarf weiterer Untersuchungen. Bei der Verrottung von Buchen-Blättern zeigt sich für die Freisetzung von Brom ein anderes Muster als bei der Weidelgras-Verrottung, was auf die Bedeutung der Eigenschaften des jeweiligen Streus hinweist.

Brom- und Jod-Konzentrationen in den untersuchten Bodenprofilen reichen von 0,6 µg/g bis 15 µg/g und die in den Bodenlösungen von 0,5µg/l bis 43µg/l. Dabei ist eine Abhängigkeit vom jeweiligen Bodenhorizont zu beobachten. Im Oberboden (reich an organischem Material) sind die Halogene bevorzugt in organischen Bindungsformen zu finden (zwischen 60 und 100%), während deren Anteil im Verlauf des Bodenprofils nach unten hin abnimmt.

Bei einem der untersuchten Waldgebiete stellt die atmospärische Deposition die Quelle für Brom und Jod dar, während im zweiten Waldgebiet eine zusätzliche Beeinflussung durch das

Ausgangsgestein festzustellen ist. Bei der Verrottung von Buchenblättern im Labor war die Bildung flüchtiger Bromver-bindungen geringer (12,9% ± 6.1) als es Berechnungen aus dem gleichen Prozeß unter natürlichen Bedingungen ergaben (24,4%). Man kann daher das Streu selbst als Quelle für Bromverbindungen ansehen.

Die vorliegende Arbeit zeigt das Vorhandensein von Halogenen in den Komponenten terrestrischer Ökosysteme, sowie deren Austausch und die Beeinflussung der Halogenverteilung und Bindungsphase durch biologische Prozesse (z.B. Wachstum, Zerfall).

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1. Introduction

1.1. Bromine in the environment

1.1.1. Introduction

Bromine was discovered in 1826 by Antoine-Jerôme Balard. It has the atomic number 35 and an atomic weight of 79.9. Bromine does not appear in nature as a free element, it is always combined with other elements, the most common salts are the bromides, organic and inorganic which are highly soluble, it is also a very volatile elements (Kabata-Pendias and Pendias, 2000; Wisniak, 2002). Bromine is at least one order of magnitude more abundant than iodine in nearly all inorganic materials (Wisniak, 2002). It is usually found at very low concentrations in fresh waters, but in sea water it is considered a major element (65 mg/l). The largest reservoir are underground waters from certain deep oil-well brines, mineral springs, and the Dead Sea (Average salinity 280 g/kg) (Wisniak, 2002). The sources (calculated for methyl bromide) include soil fumigation, automobile exhaust, biomass burning and fertilizers (Kabata-Pendias and Pendias 2000; Orlando, 2003). The estimated Methyl bromide release for soil fumigation is 41 Gg/year (Orlando, 2003). The contribution of automobile exhaust to the overall budget is minor and is estimated as 5 Gg/year while the biomass burning contributes approximately 30% of the stratospheric bromine budget (20-50 Gg/year) (Gribble, 1999).

1.1.2. Bromine in rocks

The common abundance of bromine in the earth's crust varies within the range of 0.2-10 mg/kg, being highest in argillaceous sediments (Kabata-Pendias and Pendias, 2000).

The total bromine content in the crust of the earth has been estimated to be 10^{15}-10^{16} tons or 0.00016% (Wisniak, 2002). There are only a few bromine containing minerals, all of them are silver ores such as *bromyrite* (AgBr), *embolite* [(Ag(Cl, Br)], and *iodobromite* [(Ag(Br, Cl, I)].

Shinonaga et al, 1994 reported that chlorine and bromine might behave similarly during formation of igneous rocks. Bromine concentration in major rock types is shown in Table 1.

Table 1. Bromine in major rock types (Kabata-Pendias and Pendias, 2000).

Rock type	Bromine conc. (mg/kg)
Magmatic rocks	
Ultramafic rocks	0.2-1.0
Mafic rocks	0.5-3.0
Intermediate rocks	1-4
Acid rocks	0.3-4.5
Acid rocks (volcanic)	0.2-1.0
Sedimentary rocks	
Argillaceous sediments	5-10
Shales	6-10
Sandstones	1-5
Limestones, dolomites	6

1.1.3. Bromine in soils

Research about bromine soil content is limited (Yuita, 1994). High contents of bromine have been discovered in peaty soils and very high concentrations were reported in volcanic soils in Japan (Roorda van Eysinga and van den Bos, 1998). In addition, Maw and Kempton (1982) reported that the high bromine contents found in peat and agricultural soils is mainly in an organic fraction. An emphasis on organobromine was given in Biester et al., (2004) which showed that up to 91% of bromine in peat is present in organic form. The topsoils contain more bromine than subsoils (Wilkins, 1978) and a strong correlation between soils and organic bromine has been reported for sediments and soils (Kabata-Pendias and Pendias, 2000). Wilkins, (1978) reported elevated soil bromine contents probably related to contamination and fixation by organic matter. Bromine cycles through soil organic matter and biomass (Gerritse and George, 1988).

Some fertilizers are known to contain much bromine which can eventually raise the concentration in soils. Addition of potassium fertilizers can increase the soil bromine concentration by 0.4μg/g yearly (Wilkins, 1978). The bromine in soil solution can be considerably affected by environmental conditions such as pH, temperature and moisture content (Yuita, 1991; Yuita, 1994). Despite the observed sorption of bromine to aluminum and iron hydroxides, organic matter and clay, bromine can be easily leached from soil profiles (Kabata-Pendias and Pendias, 2000).

Like iodine, bromine within soils mainly derives from atmospheric precipitation (Gerritse and George, 1988; Kabata-Pendias and Pendias, 2000).
In a fumigated methyl bromide soil, the methyl bromide is degraded to bromide. Possible reactions are the methylation of structural elements in the organic material which contain oxygen-, sulphur- and nitrogen groups, and hydrolysis while bromide ions and methanol are produced (Dimitriou and Tsoukali, 1998).

1.1.4. Bromine and health

Bromine can enter the human body through the food chain with consequences to health (Dimitriou and Tsoukali, 1998), it can cause rash, bromism, central nervous system depression, mental deterioration and acneform skin eruptions (Mino and Yukita, 2005).
The use of methyl bromide in agriculture poses a problem related to the presence of bromide in plants with a consequence to public health through the food chain (Dimitriou and Tsoukali, 1998). Application of methyl bromide as a soil fumigant can also affect animals. Bromide intoxication was reported in horses, goats and cattle after were fed with oat hay that been cut from a field treated with methyl bromide (Dimitriou and Tsoukali, 1998).

1.1.5. Bromine in terrestrial plants

Bromine is one of the most abundant and ubiquitous of the recognized trace elements in the biosphere (Mino and Yukita, 2005), it is not an essential element for plant growth but is easily absorbed by plants and occurs in almost all plant tissue (Bisessar and Mcllveen, 1992; Jemison and Fox, 1991; Magarian et al., 1998; Owens et al., 1985).
Various plants have been investigated for bromine uptake, including barley (Bowman et al., 1997), alfalfa (Bowman et al., 1997; Magarian et al., 1998), corn (Jemison and Fox, 1991), canola (Bowman et al., 1997), sorghum (Chao, 1966), ryegrass (*Lolium perenne* L.) (Schnabel et al., 1995), lettuce (Kempton and Maw, 1972), wetland plants (Xu et al., 2004), tomato (Kempton and Maw, 1973), Kentucky bluegrass (Bisessar and Mcllveen, 1992), orchardgrass-Kentucky bluegrass mixture (Owens et al., 1985) and various Japanese vegetables (Mino and Yukita, 2005). Bromine is present in halophytes about two orders of magnitude higher, compared to glycophytes, very close to 740 mg/kg (Yuita, 1994; www.usf.uni-osnabrueck.de/~hlieth/lieth). Different plants species absorb bromine differently (Tainter and Bailey, 1980) and species differ within their tolerance to the bromine concentrations in soils. Some of them are sensitive (potato, onion, spinach, sugar beet, carnation, and chrysanthemum) while other are resistant (carrot,

tobacco, tomato, celery, and melon) (Kabata-Pendias and Pendias, 2000). Natural bromine concentrations in plants vary from 1-40 ppm, and higher value may be related to pollution (Kabata-Pendias and Pendias, 2000). Bromine contents in plants can be calculated from soil water soluble bromine fraction (ratio 1:2) (Roorda van Eysinga and van den Bos, 1998). The bromine plant uptake can occur via roots (Tainter and Bailey, 1980; Wyttenbach et al., 1997) and via leaves (Paradellis and Panayotakis, 1980; Tobler et al., 1994; Wyttenbach et al., 1997). The bromine transportation mechanism from plant to soil is not studied yet (Kabata-Pendias and Pendias, 2000). Wilkins (1978) reported that bromine concentration in herbage is derived form precipitation or sea spray deposition, and not by the uptake from the soil.

Plants which have been grown on fumigated soils with methyl bromide contain more bromine (Freitas et al., 1995). Some inorganic bromine in plants is related to the breakdown of brominated fumigant products (Mino and Yukita, 2005). Levels of bromide can be elevated in plants grown in soils fumigated with methyl bromide (Dimitriou and Tsoukali, 1998). Bromine levels in cultivated plants is higher compared to wild plants due to the use of pesticides and fertilizers containing bromine (Yuita, 1994).

A linear uptake of bromine by plants is known for various ranges (Chao, 1966; Kempton and Maw, 1972; Kempton and Maw, 1973; Magarian et al., 1998; Xu et al., 2004) and nitrogen fertility can significantly affect the uptake (Schnabel et al., 1995). The uptake of bromine and NO_3^- is linear (under field conditions) suggesting that bromine can indicate relative efficiency of NO_3^- uptake in crop management experiments. Regardless to that, it is not recommended to study NO_3^- uptake using bromine due to the probability that the uptake mechanisms are different (Magarian et al., 1998).

Bromine can substitute parts of the chlorine plant requirements (Kabata-Pendias and Pendias, 2000) but chlorine inhibits bromine uptake by plants, emphasizing the importance of chlorine in plant physiology (Xu et al., 2004).

Bromine concentrations in herbage according to Wilkins (1978) do not correlate with bromine soil concentrations and soil properties (pH, type, drainage status). Although in a limited study Schnabel et al., (1995) showed that bromine uptake is significantly smaller in poorly drained soils compared to well drained soils.

Bromine plant concentration in some plants can be a very sensitive indicator to bromine environment levels (Wyttenbach et al., 1997). Lead and bromine content in lichen samples showed correlation which is a result of use/presence of both of them in gasoline (Garty et al., 1985). *Populus* spp. bromine concentrations in the 1980s were related to bromine air concentrations caused by city traffic (Paradellis and Panayotakis, 1980). Dibromoethane was an

additive of leaded gasoline, and organobromine compounds ,especially methyl bromide, were found in exhaust gases (Tobler et al., 1994).

Examination of healthy *T. latifolia* and *P. australis* plant parts (leaf, stem, and root) revealed that bromine was in inorganic form. Furthermore, the absolute intensity of the bromine signal in the spectra of the plant leaves was 2.5-4 times greater than that in the roots and stems, indicating that the leaves had the highest bromine concentrations. However, the difference in density and thickness of the samples makes a bromine quantitative estimation problematic (Xu et al., 2004).

Bromine is used as hydrologic tracer because of its low background concentration in most soil solutions, since it is assumed to have low biological and chemical reactivity in soil environments (Owens et al., 1985; Schnabel et al., 1995; Whitmer et al., 2000; Xu et al., 2004), Further studies showed that plants can accumulate bromine above the low biological reactivity concentrations from the root zone (Schnabel et al., 1995) and due to that, bromine should be used cautiously as a hydrological tracer in long term field experiments (Schnabel et al., 1995).

1.2 Iodine in the environment

1.2.1 Introduction

Iodine was discovered in 1811 by Coutrios though sublimation of the element from seaweed ash, using sulfuric acid. It has the atomic number 53 and an atomic weight of 126.9. The iodine anionic radius is rather big (2.20 Å) and in many biomolecules it can replace other groups. The chemistry of iodine is quite complex due to the many oxidation states; -1, 0, +1, +3 and +5. Iodide (I^-) and iodate (IO_3) are the most important inorganic ions to be found in the biosphere. Beside inorganic iodine compounds there are also many organic iodine compounds and some of them are synthesized by biological activity (Fuge and Johnson, 1986; Whitehead, 1984).

There is only one stable isotope of iodine, ^{127}I, but more than 20 radioactive isotopes. Among them ^{131}I has a half life of 8.04 days while ^{129}I has a long half-life of $1.7 \cdot 10^7$ years. From radioecological point of view ^{129}I and ^{131}I are considered to be the most important since they are released from nuclear weapons and facilities (Muramatsu et al., 1989; Yuita, 1994). Furthermore, radioactive iodine, mainly ^{125}I and ^{131}I, are used in many cellular biological laboratories (Narra et al., 1992) to label biomolecules since iodine easily reacts with many biomolecules particularly those with unsaturated bonds or ring structures.

Global distribution of iodine is depicted in table 2 (Whitehead, 1984). Typical concentrations of iodine in various components of the environment are shown in Table 3.

Table 2. Iodine global distribution (Whitehead, 1984).

Component	Mass (g)	Concentration of iodine (mg/kg)	Global amount of iodine (kg)
Earth's crust	$24 \cdot 10^{21}$	0.14	$3.4 \cdot 10^{15}$
Sedimentary rock	$7.2 \cdot 10^{21}$	0.4	$2.9 \cdot 10^{15}$
Hydrosphere	$1.42 \cdot 10^{21}$	0.06	$7 \cdot 10^{13}$
Atmosphere	$5.3 \cdot 10^{18}$	$1 \cdot 10^{5}$	$4 \cdot 10^{7}$
Biosphere	$1.8 \cdot 10^{16}$	0.05	$9 \cdot 10^{8}$
Annual transfer in rainfall	$104 \cdot 10^{15}$	0.004	$4.2 \cdot 10^{8}$

Table 3. Typical concentrations of iodine in various components of the environment (on a dry weight basis for the solid material) (Whitehead, 1984).

Components	Iodine concentration	Unit
Igneous rocks	0.08–0.50	mg/kg
Sedimentary rocks	0.2–10.0	mg/kg
Marine sediments	3–400	mg/kg
Soils	0.5–20	mg/kg
Seawater	45–60	µg/l
Rainwater	0.5–5.0	µg/l
River and lake water	0.5–20	µg/l
Atmosphere	10-20	ng/m^3
Higher plants	0.05–0.5	mg/kg
Marine algae	90–2500	mg/kg
Mammalian tissue	0.05–0.5	mg/kg
Marine fish (soft tissue)	0.5–6	mg/kg
Freshwater fish	0.06–0.2	mg/kg
Coal	1–15	mg/kg

1.2.2 Iodine content in rocks

Iodine content in common rocks differs between various rock types.

Igneous rocks: As shown in Table 2 the iodine concentrations in igneous rocks range between 0.08–0.50. Detailed review by Fuge and Johnson (1986) showed that there is no significant

difference in between the iodine abundance in intrusive and extrusive rock igneous rocks and the iodine concentration mean is 0.24 mg/kg.

Sedimentary rocks: Sedimentary rocks contain more iodine than igneous rocks with a wider range of values, the mean value is 2 mg/kg (Fuge and Johnson, 1986). The range of value indicates that recent sediments (5-200 mg/kg) contain more iodine then carbonates (2.7 mg/kg) as well as shales (2.3 mg/kg) and sandstone (0.8 mg/kg). Again, the data is more concise compared to table 2.

Recent measurements of iodine concentration in rocks indicate that sandstone contain 0.05-0.33 mg/kg, limestones 0.26-3.87 mg/kg and shales rich in organic carbon 0.41-6.15 mg/kg (Muramatsu and Hans Wedepohl, 1998). The main reservoirs of the crust's iodine were found to be marine sediments and sedimentary rocks (Muramatsu et al., 2004).

Iodine is a minor constituent of various minerals but does not form any separate minerals. Iodine in minerals include iodides of some metals such as AgI, CuI, $Cu(OH)(IO_3)$, polyiodates, iodates and periodates (Kabata-Pendias and Pendias, 2000).

1.2.3 Iodine in rain

The iodine content in rain and snow range between 0.5-20 µg/l without any significant difference between snow and rain, although it is expected that snowflakes will have higher capacity to adsorb atmospheric iodine due to its bigger surface area (Fuge and Johnson, 1986).

The iodine source in atmospheric deposition is from oceanic emission of iodine compounds which are transported to terrestrial area (von Glasow and Crutzen, 2003; Lovelock et al, 1973).

Results published by Krupp et al., (1999) indicate that a long-distance atmospheric transport of iodine to Germany can be from the Atlantic Ocean as well as from the North Sea. The iodine species transported through long distance are mainly organically bound iodine and secondly particulate bound iodine. The organoiodine and the secondly particulate bound iodine species can be created over the terrestrial environment when plant VOC emissions and VOCs oxidations products (gas to particle conversion) (Kroll et al., 2006) react with iodine.

1.2.4 Iodine in soil

Soil is probably the largest accumulator for iodine and its isotopes within the terrestrial environment and contributes iodine to plants and groundwater via percolating water.

Iodine concentration in soil is much higher than in its parent materials due to versatile sources (Gerzabek et al., 1999; Kabata-Pendias and Pendias, 2000; Muramatsu et al., 1996). The sources of iodine in the environment include:

Atmospheric deposition: It is the predominant source. In continental regions where deposition is low, other sources can be a significant contributor (Carpenter, 2003; Fuge and Johnson, 1986; Gerritse and George, 1988; Kabata-Pendias and Pendias, 2000; Kolb, 2002; Kronberg et al., 1987; O'Dowd et al., 2002; Whitehead, 1984). However, halogen concentration in wet and dry depositions are affected by various factors, such as chemical form, distribution between gaseous and particulate form, different species of the gaseous, different size of the particulate, meteorological conditions and land surface properties (Whitehead, 1984). The iodine concentrations in soil do not decrease with increasing distance from sea coast, some inland soils have more iodine compared to coastal soils. This is expected since total annual deposition of iodine by rainfall is higher at the inland sites than near the cost due to heavier rainfall at inland sites (Schnell and Aumann, 1999).

Subsurface formation waters and mineralizing brines: Several reports indicate that in arid areas subsurface waters leads to accumulation of iodine in soils (Fuge and Johnson, 1986).

Bedrock material: Soils are richer than the rocks they are formed form. It is difficult to explain the enrichment of iodine in soil solely because of parent material contribution. Although some research claims parent material iodine is a source (Cohen, 1985). Fleming (1980) declared that atmospheric deposition is the main iodine source.

Agricultural sources: Certain chemicals and fertilizers contain iodine that might result in increased concentration in agricultural soil (Whitehead, 1984).

Iodine content varies between soil types and an exampled data is shown in Table 4. The iodine can be present in three phases: mobile iodine, insoluble iodine and fixed iodine (Fig. 1).

Table 4. Iodine content of U. K. soils (0–15 cm) derived from nine categories of parent material (Whitehead, 1978).

Category of parent material	Interval (mg/kg)	Mean value (mg/kg)
Acid igneous rocks and associated till	4.4–15.7	10.4
Till associated with basic igneous rocks	3.4–16.3	10.9
Slate, shale and associated till	4.4–27.6	9.8
Sand and sandstone	1.7–5.4	3.7
Chalk, limestone	7.9–21.8	13
Clay	2.1–8.9	5.2
River, and river terrace, alluvium	0.5–7.1	3.8
Marine and estuarine alluvium	8.8–36.9	19.6
Peat	18.7–98.2	46.8

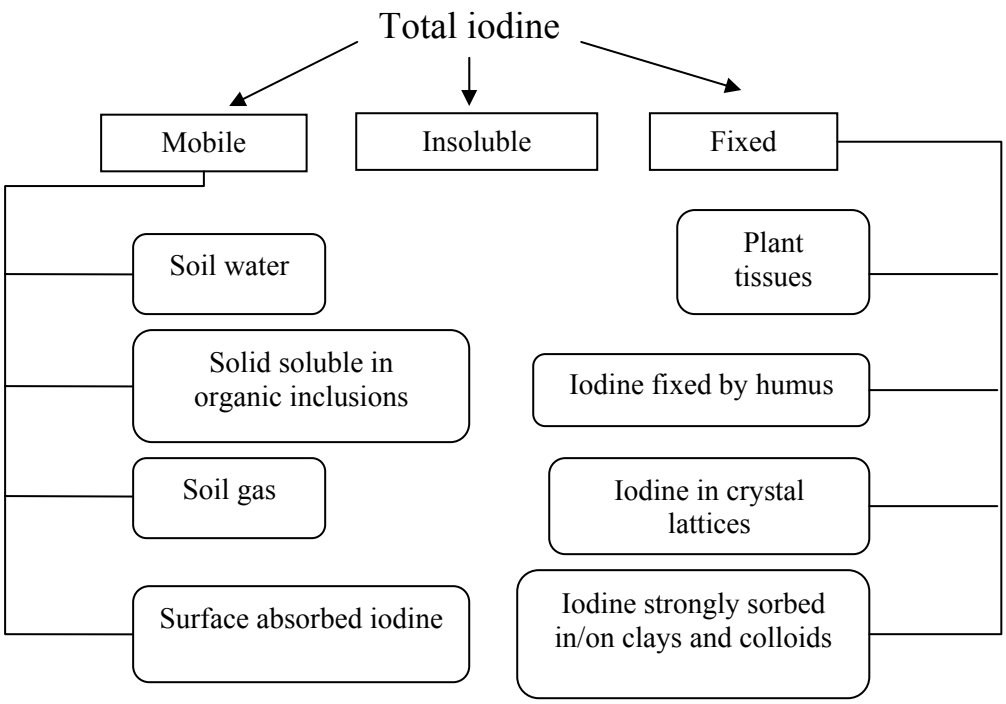

Fig. 1. Suggested iodine forms in soil (Fuge and Johnson, 1986).

Several ionic forms such as I^-, IO_3^-, I_3^-, IO^-, IO_6^{3-}, $H_4IO_6^-$ as well as organoiodine compounds can exist in the soil aquatic phase but the first two (iodide and iodate) are the most common ones (Kabata-Pendias and Pendias, 2000; Yamada et al., 1999). Sorption of iodide and iodate may occur quickly, and decreases as pH increases, as expected by the general rule of anion sorption (Sheppard et al., 1996). Association between iodine and organic matter, hydrous oxides of iron

and aluminum as well clay, have been documented in various studies (Fuge and Johnson, 1986; Hou et al., 2003; Kabata-Pendias and Pendias, 2000; Sheppard and Thibault, 1992; Whitehead, 1973a; Whitehead, 1974; Whitehead, 1978; Whitehead, 1984; Xiangke et al., 1999; Xiangke et al., 2001; Yuita, 1992). However, some works reported that organic matter is mainly responsible for iodine sorption in soil and therefore it is accumulated largely in topsoil horizons (Amachi et al., 2001; Gerzabek et al., 1999; Kabata-Pendias and Pendias, 2000; Kaplan, 2003; Sheppard and Thibault, 1992; Sheppard et al., 1996). It is known that humic acid plays an important role in iodine fixation in soils and aquatic environments (Gerzabek et al., 1999; Grøn and Raben-Lange, 1992; Mercier et al., 2000; Sheppard and Thibault, 1992). Chlorine is known to interfere with iodine sorption, suggesting that anion exchange is a major factor in iodine retention (Sheppard et al., 1996). Organohalogens are omnipresent in the environments and most of them are stored in soils (Asplund, 1995).

Peat bogs are known to contain organoiodine compounds up to 81% of the total iodine. The estimated amount of iodine in peatlands is 12-36 teragrams, suggesting that peatlands are a major reservoir in the terrestrial ecosystems (Biester et al., 2004; Keppler et al., 2004).

Iodine can be lost from soils via different mechanisms:

Mechanical and chemical transport: Iodine can be removed from soils by means of water movement which will cause vertical and horizontal migration. However, possible removal of iodine and specific fractions which are responsible for fixing iodine (e.g. organic matter) as considered by Fuge and Johnson (1986).

Volatilization: The most significant feature of the global iodine cycle is its volatilization into the atmosphere (Fuge and Johnson, 1986). It has been suggested that volatile iodine species (mainly organic iodine) can enter the troposphere and even the lower stratosphere by convective transport, affecting the atmospheric ozone (Amachi et al., 2003). Wide varieties of terrestrial bacteria are capable for methylating iodine (Amachi et al., 2001; Muramatsu et al., 2004) but bacterial CH_3I production depends greatly on the surrounding iodine levels (Amachi et al., 2001). A possible change in the condition of the soil solution or microbial community may affect CH_3I emissions since variations of CH_3I concentrations in duplicate measurement became larger with time (Amachi et al., 2003).

When soil samples were incubated with a specific antibiotic which inhibits prokaryotes growth (streptomycin and tetracycline), iodine volatilization was completely prevented. Specific antibiotics for eukaryotes (cycloheximide) did not cause any significant inhibitory effect (Muramatsu et al., 2004). These results suggest that soil bacteria (mainly, aerobic soil bacteria) may preferentially contribute to iodine volatilization from soil environments (Amachi et al.,

2003; Muramatsu et al., 2004). Limited data is available regarding halogen methylation capabilities by fungi (Redeker et al., 2004a).

The extrapolation of the results to natural soil environments is, however, difficult because of the dependence of iodine availability on the properties of soils and the large variations in iodine levels among different soil types (Amachi et al., 2001).

Crop: Cropping of soil is responsible for removing up to 620 $\mu g/m^2$, however this phenomenon only takes place in environments, where iodine sources are low. In agricultural areas a compensation between cropping and iodine containing fertilizers and humus might occur, resulting little or no loss of iodine (Fuge and Johnson, 1986).

1.2.5 Iodine and health

Iodine is an important trace element for mammals including humans and an essential substrate for the synthesis of thyroid hormones (Delange, 1998). The two major thyroid hormones are triiodothyronine (T3) and tetraiodothyronine (T4) (Kung et al., 2001; Yuita, 1994). The human body needs about 100-150µg iodine every day (Huan-xin et al., 2003; Mackowiak and Grossl, 1999; Shinoyama et al., 2001) and the main consumption sources by humans are sea food and milk products (Shinoyama et al., 2001).

Iodine deficiency is a major threat to the health and development of populations worldwide. Lack of sufficient iodine supply may result a series of functional and developmental abnormalities, collectively referred to as iodine deficiency disorders (IDD). Conditions related to iodine deficiency include goiter, stillbirth and miscarriage, hypothyroidism, mental and neurological disorders and impaired growth (Andersson et al., 2005). Universal salt iodization (USI), defined as iodization of all salt used for human and animal consumption, is the main strategy used to control iodine deficiency. Globally, 66% of households now have access to iodized salt (Andersson et al., 2005). However, the most serious and common complication of salt iodization is the development of iodine-induced hyperthyroidism (IIH) (Delange, 1998). In Fig. 2 a map that is classified by the six degrees of public health significance with respect to their iodine intake estimated from median urinary iodine is shown (Andersson et al., 2005).

The impact of iodine methylation should also be considered from the viewpoint of the hazard posed by anthropogenic ^{129}I. Once it is methylated, ^{129}I can spread far from a contaminated area and may accumulate in the human thyroid gland (Amachi et al., 2001).

Fig. 2. Degree of public health significance of iodine nutrition based on median urinary iodine (Andersson et al., 2005).

1.2.6 Iodine in terrestrial plants

Essentiality of iodine to plants has not been confirmed (Kabata-Pendias and Pendias, 2000; Whitehead, 1984; Yuita, 1994) and iodine is not believed to perform any metabolic function in plants and low iodine soil levels do not inhibit the growth (Fuge and Johnson, 1986). Terrestrial plants contain much less iodine compared to marine plants (algae), which can accumulate iodine from 53-8800 mg/kg based on dry weight (Kabata-Pendias and Pendias, 2000).

There are two main transfer pathways for iodine from the environment to the plant. By atmospheric deposition, both through the cuticle/stomata as well as adhesive particles on the surface of hairy leaves, and by soil uptake (Kabata-Pendias and Pendias, 2000; Oestling et al., 1989; Whitehead, 1984)

Iodine concentrations in plants changes due to seasonal variation (Alderman and Jones, 1967; Aller et al., 1990; Hartmans, 1974; Smith et al., 1999), plant type (Hartmans, 1974; Huan-xin et al., 2003), species differences (Alderman and Jones, 1967; Dai et al., 2004; Fuge and Johnson, 1986; Huan-xin et al., 2003; Whitehead, 1984) and leaf surface properties (Whitehead, 1984). Iodine content in plants can also be a result of its inherited character (Alderman and Jones, 1967; Hartmans, 1974). Compared to other halides, plants accumulate low levels of iodine, similar to

those of fluorine, rather than high concentrations of bromine and chlorine (Whitehead, 1975). The concentration in plants increase as the soil or soil solution content increases (Aller et al., 1990; Huan-xin et al., 2003; Mackowiak and Grossl, 1999; Whitehead, 1973b) and the iodine form present within the root surface (Mackowiak and Grossl, 1999). Humic acid/organic matter reduce iodine bioavailability and reduce its toxicity in high concentration (Mackowiak et al., 2004; Whitehead, 1984). Various higher plants are affected differently by iodine disinfection products (Janik et al., 1989).

Iodine concentrations in plants are higher when iodide and not iodate is used (Smith et al., 1999; Whitehead, 1973b). It seems that iodate needs to be reduce to iodide before uptake (Cseh and Böszörmenyi, 1964; Whitehead, 1973b). The toxicity of iodine to higher plants is stronger then other halogens (Yuita, 1994) and the iodine species toxicity order is $I_{2(aq)} > I^- > IO_3^-$ (Mackowiak et al., 2004). Chloride does not affect iodine uptake even when it is supplemented in high concentrations (Whitehead, 1973b) and bromine does not depress iodide uptake (Whitehead, 1984).

Plants have a limited adsorbing capability (Huan-xin et al., 2003), respond differently to increasing iodine in soil (Dai et al., 2004) and high level of iodine can be detrimental to yields (Zhu et al., 2003). Iodine toxicity is responsible for the "Reclamation Akagare" that occurs in rice plants grown on newly reclaimed paddy soils (Watanabe and Tensho, 1970; Yuita, 1994). The affected plants show higher iodine concentrations compared to normal plants. the toxicity is related to the ability of iodide to be bound to a number of cellular components, including chlorophyll, consistent with intracellular oxidation of the iodide (possibly by the plant peroxidase system) (Aller et al., 1990; Mynett and Wain, 1973). The toxicity symptoms are margin chlorosis in older leaves, necrosis in leaf tips and dark green color in younger leaves (Aller et al., 1990; Mackowiak and Grossl, 1999). Iodide ion, either as an inorganic salt or organic complex, promotes leaf abscission (Herrett et al., 1962). Iodine tends to accumulate in dead or senescent parts of the plant (Whitehead, 1973b).

The channel of iodine entering through the soil to vegetable body is the root hair, rhizome, leaf blade (Huan-xin et al., 2003). Although iodine is regarded non-essential for plants its uptake is not only by passive means with water transpiration (Whitehead, 1973b). The low accumulation of iodine in grains points out that iodine is not mobile in the phloem (Herrett et al., 1962; Mackowiak and Grossl, 1999; Whitehead, 1984; Zhu et al., 2003). In addition, the amounts of iodine and edible fruit tissue (tomatoes, bananas, melons and strawberry) are usually minimal, and higher in other plant parts (Mackowiak et al., 2004). There are considerable differences in iodine content among plant organs as shown in Table 5.

Table 5. Content of iodine in plant organs (Yuita, 1994).

Organ	No. of samples	Iodine content (mg/kg)	
		Average	Min.-Max.
Leaves	177	0.46	0.029-2.2
Fruits	32	0.14	0.006-1.7
Edible roots	7	0.055	0.02-0.18
Seeds	10	0.0039	0.00094-0.01

Some studies indicate that plants accumulating more iodine in leaves than in roots (Zhu et al., 2003) while others indicate the opposite (Whitehead, 1984). Leaves and stems of vegetation are major accumulators for ^{129}I but small amounts are translocated into the root (Ghuman et al., 1993).

Jopke et al., (1996) suggested to supply enriched iodine plants as a prophylactic against iodine deficiency (IDD) beside iodized salt. However, iodine enriched plants by means of foliar uptake or using fertilizer do not appear to be of practical importance (Kabata-Pendias and Pendias, 2000).

Based on various works (Schmitz and Aumann, 1994) radiological assessments of ^{129}I release from nuclear facilities should not be based on soil-to-plant transfer factors derived from ^{127}I data. Since iodine transfer factors vary largely, their should be used with caution for analysis and applied use (Ban-Nai and Muramatsu, 2003).

1.2.7 Importance of iodine

In the introduction given above, iodine was shown as an important element in environmental biogeochemistry. It is essential for animals and human health, involve in atmospheric chemistry, emitted from anthropogenic and natural sources, abundant in the environment. Nevertheless, the biogeochemical cycle of iodine is not fully deciphered and furthermore the influence of terrestrial ecosystem in the cycle is not sufficiently known. Further studies are need to fill and understanding the known gaps of this complex element.

1.3 Organobromine and organoiodine in the terrestrial environment

More than 3800 organohalogen compounds, mainly containing chlorine or bromine and just few with iodine and fluorine, are produced by living organisms or are formed during natural

abiogenic processes, such as volcanoes, forest fires, and other geothermal processes (Gribble, 2003). Interest in halogen sources form terrestrial environment has increased since halogens are known to cause ozone depletion. In addition, there is an imbalance between calculated emissions from known sources and the estimated global sink of methyl halides (Butler, 2000; Harper and Hamilton, 2003). The oceans are the single largest source of biogenic organohalogens (Scarratt and Moore, 1996), which are biosynthesized by a variety of marine organisms. The functions of organohalogens are varied, and they can have distinct physiological or biochemical roles (Murphy, 2003). Terrestrial plants, fungi, lichen, bacteria, insects, some higher animals, and even humans also account for a diverse collection of organohalogens (Gribble, 2003).

Terrestrial plants: Terrestrial plants are relatively devoid of halogenated compounds, and there are few exceptions like growth hormone (4-chloroindole-3-acetic acid) (Gribble, 2003). Halomethanes (methyl iodide and methyl bromide) have been studied in several plant sources. Methyl bromide, a commercial fumigant and nematicide (Dimitriou and Tsoukali, 1998; McDonald et al., 2002), is produced by many plants like *brassica* plants (e.g. broccoli, cabbage, mustard, pak-choi, radish, turnip, and rapeseed) (Gan et al., 1998), and also other plants can uptake methyl bromide form the atmosphere (Jeffers et al., 1998). Rice (*Oryza sativa* L.) is a well researched plant that has been shown to release and uptake halomethanes (Redeker, 2000; Redeker et al., 2004b; Redeker et al., 2004c). The behavior of the halomethanes in plant is affected in-between species, season, plant parts, growth period and physicochemical parameters (Collines et al., 2004; Lee-Taylor and Redeker, 2005; Muramatsu and Yoshida, 1995; Redeker et al., 2004b; Redeker et al., 2004c). Genetic analysis of the plant *Arabidopsis thaliana* indicates that the ability of vascular plants to emit halomethanes is widespread and related to methyl transferase enzymes (Rhew et al., 2003). Methyl transferase enzymes transfer a methyl group from S-adenosylmethionine (SAM) to a halogen as shown in Fig. 3. Some of these enzymes are quite labile, making purification and characterization difficult, but kinetic measurements indicate that the preference of halides is $I^- > Br^- > Cl^-$, although the concentration of halide ions in the environment probably determines the proportions of the halomethanes eventually produced by the organism (Manley, 2002; Murphy, 2003).

Gribble (2003) concludes that "given the ubiquitous distribution of bromide in soil, methyl bromide production by terrestrial higher plants is likely a large source for atmospheric methyl bromide". Estimation of methyl bromide from terrestrial sources is limited resulting that further studies are required in order to quantify the terrestrial contribution.

Fungi and lichen: These organisms can produce a variety of organohalogens, both simple and complex compounds (Gribble, 2003). Basidiomycetes (e.g. white rot and brown rot fungi) are higher fungi that play important ecological roles in the recycling of nutrients, decomposing plant

debris and are important producers of organohalogen compounds. White rot fungi are unique in their ability to attack the natural aromatic polymer lignin in wood with extracellular oxidative enzymes (Field and Wijnberg, 2003). Lee-Taylor & Holland (2000) explored numerically the possibility of methyl bromide emission form decomposed plants by wood-rotting fungi and indicated that the potential flux is 0.5-5.2 (1.7) kT/year. During decomposition process from plant leaves to decomposed organic matter, the iodine concentration increase markedly and bromine concentrations increase slightly, respectively (Yuita, 1994).

Ectomycorrhizal fungi which are common globally (especially in temperate forests, where they can constitute an estimated 15% of soil organic matter) have shown to be able to emit methyl halides (Redeker et al., 2004a). Redeker et al. (2004a) indicate that caution should be applied when considering the Lee-Taylor & Holland (2000) extrapolation efforts, since the relative efficiency of different methyl halides conversion appears to vary among species and even within morphotypes of the same species.

Bacteria: These single-celled organisms can synthesize various organohalogens. More than fifty *Streptomyces* species have yielded organohalogen metabolites. The bacterium *Amycolatopsis orientalis* produces the life-saving glycopeptide antibiotic vancomycin, which has been used for nearly 50 years to treat penicillin-resistant infections (Gribble, 2003).

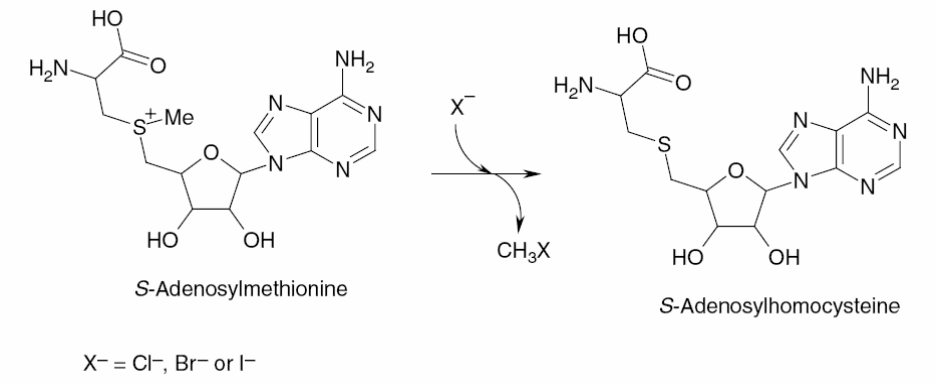

Fig. 3. Reaction catalyzed by S-adenosylmethionine: halide ion methyl transferase (Murphy, 2003).

Abiogenic Sources: Natural combustion sources such as biomass fires, volcanoes, and other geothermal processes account for a wide range of organohalogens. The halocarbons abiotic formation during diagenesis processes is show in Fig. 4.

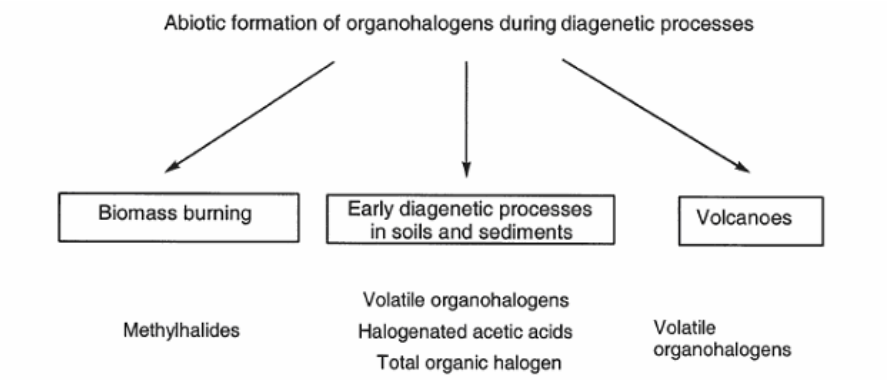

Fig. 4. Scheme of the abiotic formation of organohalogens in the terrestrial environment (Schöler and Keppler, 2003).

Biomass burning: in this process radical chemistry of organic material in the presence of halides at elevated temperatures results in methyl halides (Schöler and Keppler, 2003; Scholes and Andreae, 2000).

Volcanoes: Versatile volatile organohalogen compounds are created via radical chemistry starting from basic carbon molecules (methane, ethene and ethyne) in the presence of halides on very hot mineral surfaces (Schöler and Keppler, 2003).

Early diagenetic processes: Although most of the organoiodine and organobromine are claimed to be formed by biotic processes there are recent studies concerning a major contribution from abiotic processes. Keppler et al., (2000) suggested that methyl halides are formed during degradation of organic matter by an oxidant (e.g. Fe^{3+}) in the presence of halide ions. The schematic process is shown in Fig. 5.

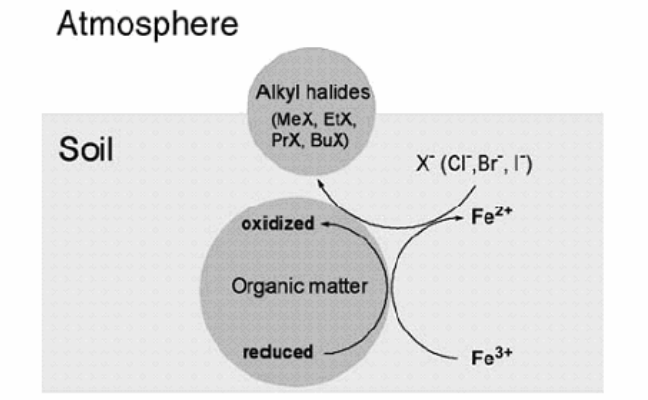

Fig. 5. Model for alkyl halide formation by the reaction of Fe^{3+} and organic matter in the presence of halide ions (Keppler et al., 2000).

Dehalogenation: The ubiquity of organohalogens in nature resulted that microorganisms which inhabit terrestrial and aquatic environment have developed mechanisms to degrade them. The reactions can occurs in aerobic and anaerobic environments and may contain several steps.

Various dehalogenation reactions are known and examples for few of them are explained (Fetzner, 1998; van Pée and Unversucht, 2003):

Hydrolytic Dehalogenation: a simple reaction where a nucleophilic substitution of halide ions by water occurs, shown in Fig. 6.

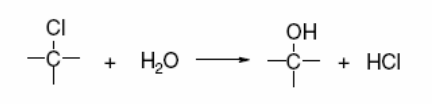

Fig. 6. Hydrolytic dehalogenation.

Thiolytic dehalogenation: The mechanism was shown in methylotrophic bacteria grown with dichloromethane as a substrate. The bacteria produce glutathione S-transferase which catalyzes the formation of an unstable S-chloromethyl glutathione intermediate. This intermediate is hydrolyzed to glutathione, chloride, and formaldehyde.

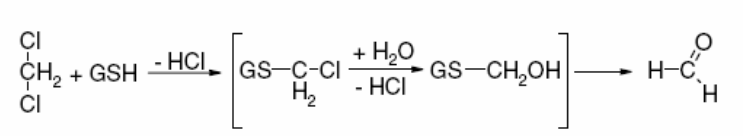

Fig. 7. Thiolytic dehalogenation of dichloromethane catalyzed by a glutathione transferase.

Dehydrohalogenation: Dehydrohalogenases eliminates HCl from their haloorganic substrate leading to a creation of double bond as shown in Fig. 8.

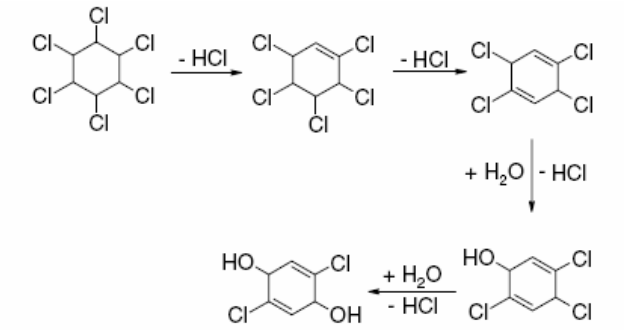

Fig. 8. Dehalogenation of lindane.

Dehalogenation by methyl transfer: Dehalogenation by methyl transfer was found in aerobic and strictly anaerobic methylotrophic bacteria while using organochlorines as their sole carbon source. Chloromethane or dichloromethane are known to support growth of strictly anaerobic bacteria. In Fig. 9. Cobalt accepts the methyl group.

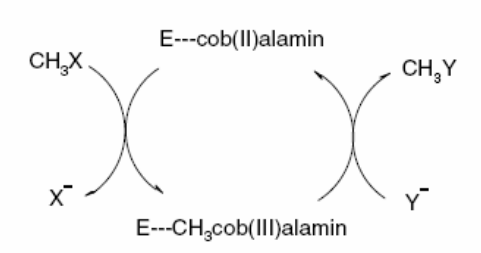

Fig. 9. Dehalogenation of chloromethane catalyzed by a cobalamin-containing methyltransferase (CH_3X can be CH_3Cl, CH_3Br or CH I, and Y^- can be Cl^-, Br^-, I^- or HS^-).

Oxidative dehalogenation: The reactions are important in biodegradation of both haloaliphatic and haloaromatic compounds. The enzymes usually involved, are monooxygenase and dioxygenase.

Reductive dehalogenation: This process can occur in anaerobic or aerobic conditions. The enzymes involved in this process are versatile and differ between organisms.

1.4 Litter decomposition

1.4.1 Introduction

The study of decomposition is an interdisciplinary science which involves aspects of many fields like: ecology, soil sciences, plant physiology, biochemistry, agriculture, forestry, microbiology, climatology, etc. The aim of this section is to introduce basic ideas, techniques and applied techniques in geosciences.

Decomposition is a complex and multi-step process of litter breakdown through leaching, mechanical and invertebrate fragmentation and transformation through the activity of soil microorganism (Swift et al., 1979). Litter decomposition is an important soil biological process regulating nutrient cycling and soil fertility (Gupta and Malik, 1999).

Decomposition is comprised of three major steps:

Leaching: The removal of soluble compounds from the detritus by water, and is particularly significant in the early stage of decomposition when nutrients and soluble material are still present.

Fragmentation: The process where litter is changing to small pieces caused by physical action and the action of the soil fauna. The process accelerates leaching and catabolism.

The chemical transformation: Transformation of complex materials (catabolism) to simpler molecules provides energy to the consumer (decomposer) (Couteaux et al., 1995). Among the decomposing compounds, lignocelluloses is the predominant component of litter which consists of cellulose, hemicellulose, and lignin (Gupta and Malik, 1999).

1.4.2 Factors affecting decomposition processes

The decomposition rate is regulated and affected by three main driving variables (Cotrufo et al., 2000; Swift et al., 1979):

Physicochemical environment: Macroclimatic variables (e.g. temperature, precipitation) and microenvironment characteristics (e.g. pH).

Resource quality: The concept of resource quality is often difficult to define, as it contains chemical and physical properties of litter material. It is generally described as the relative decomposability of litters, depending on the relation between labile and recalcitrant compounds, which defines the nature of energy source, concentration of nutrients and modifier compounds and the physical structure of the decomposing substrate (Cotrufo et al., 2000). Litter quality generally decreases during the course of decomposition due to the loss of readily available C and the accumulation of refractory compounds (Dilly et al., 2004).

Decomposer organisms: Plant material is largely mediated by fungi and bacteria, which have lower C/N ratio then the litter and therefore have high demand for nitrogen. Other microorganisms that are involved in the process are shown in Fig. 10.

The soil fauna contributes actively to litter breakdown by: grinding plant residues and increase their surface area, mixing soil organic matter with the soil horizon and channeling and improving the soil structure (Couteaux et al., 1995).

The linkage between plant quality, soil biota, physico-chemical environment and the decomposition processes are important (Swift et al., 1979).

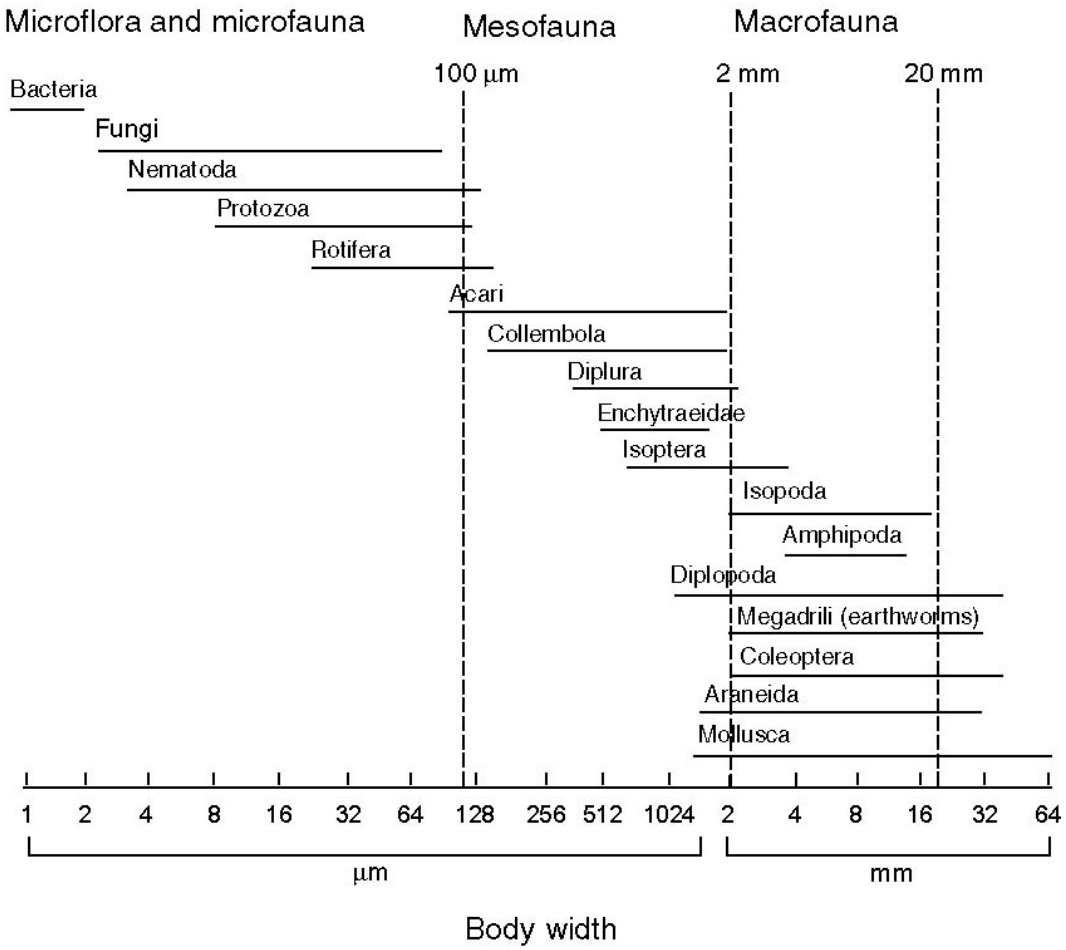

Fig. 10. Size classification of organisms in decomposer food webs by body width (Swift et al., 1979).

1.4.3 Techniques used in decomposition studies

Decomposition is been studied for years and during this time several methods were developed (Gupta and Malik, 1999):

Litterbag: Litter bag is the most common technique for the examination of decomposition rates. The method has been used to compare species, sites and experimental manipulation. The litter is placed in a nylon bag with a define mash and usually buried in the soil. After different time intervals the bag is retrieved and analyzed for dry mass, moisture content, ash content and nutrients composition. The decomposed litter often shows soil contamination which requires a correction based on percent litter mass remaining on an ash-free dry weight basis. During rinsing some loss of water soluble materials occurs but it can also be measured. Litter bag technique provides useful information on decomposition rates in relation to climatic seasonality, resource quality and the role of leaching and soil fauna.

Litter Basket: The technique allows studying the interaction between fauna, microbes and litter quality. A litter baskets (10x10x10 cm) made from hardware cloth with 6 mm mesh and a plastic

window screen (mesh 1.5x1.8 mm) separates the forest floor profile (soil and litter). The baskets are collected over time and are analyses for litter decay rate, patterns of nutrient immobilization/mineralization. Microarthropods, bacteria, fungi and nematodes are enumerated. The method has few advantages such as reducing microclimatic effects, allows use of isotopes and easy extraction of biota.

^{13}C Nuclear Magnetic Resonance (NMR): The latest technique applied was developed in the recent years. Solid state ^{13}C NMR spectroscopy offers the possibility of direct characterization of organic material in intact soils or fractions of it. The plant tissue compounds have different spectral bands and they can be followed during degradation of particular type of plant tissue (Wershaw et al., 1996). The technique is non destructive and does not cause any chemical alteration.

The fate of specific elements in decomposition is a key factor in understanding the processes involved. Radioisotopes are a convenient way to investigate the loss of elements by leaching, fragmentation and transformation. The techniques limits are related to the half-life of the isotopes and their biological activity (Gupta and Malik, 1999; Swift et al., 1979).

Tagging techniques: Tagging organic debris with a radioisotope is a convenient way to measure loss of litter and nutrients release during decomposition. The method is not efficient in small leaves with a longer decay rate than the radioisotope decay rate.

^{14}C techniques: ^{14}C has been used to label decayed plant material and analysis of residual carbon addition.

^{13}C stable isotopes techniques: Due to the limiting measurement of ^{14}C under field conditions ^{13}C has been used increasingly. The turn over of organic matter can be studied using the $^{13}C/^{12}C$ ratio.

Biological activity in litter decomposition can be quantified using several methods (Gupta and Malik, 1999):

Respirometric technique: Heterotrophic soil organisms degrade litter and the end products of the aerobic degradation process are carbon dioxide and water. The overall metabolic activity of soil organisms can be determined by monitoring the CO_2 increase or O_2 depletion.

^{14}C-CO_2 evaluation rates: The idea of the technique is similar to the previous one but the use of radioisotope requires different techniques in order to measure the ^{14}C-CO_2.

Enzymatic activates: Enzymatic index of carbon quality as the ratio of cellulose activity to ligninase activity (the ratio of hydrolytic to oxidative enzyme activity) was found to be highly correlated with decomposition rates.

N mineralization from decomposing litter: The method allows assessing the nitrogen mineralization under controlled conditions. The use of ^{15}N as becomes an important tool in order to estimate N mineralization.

1.5 Study objective

The main objective of the studies was to investigate the natural enrichment processes of bromine and iodine in terrestrial environment. In order to achieve this aim, bromine and iodine behavior, distribution and speciation in this environment, especially in plant-soil systems. The experiments were performed under laboratory conditions as well as in the field.

The laboratory experiments aims was to study the fate of bromine and iodine during plant life cycle, from seed to decomposition, to quantify the uptake of the examined halogens by plants and to study their release and speciation during decomposition. The approach was to grow a model plant with supplemented halogen in hydroponic solution. Annual ryegrass (*Lolium multiflorum)* was chosen as the model plant due to its high yield potential and fast establishment. In addition, Atlantic beech (*Fagus Sylvatica*) leaves were collected from one of the field sites and decomposed in order to examine naturally grown leaves.

The field study was to examine the distribution, behavior and speciation of bromine and iodine in forest soils and to identify the possible halogen sources in the research area (atmospheric deposition, parent material) and to understand the possible interconnection between the environment components. The study comprise inspection of halogen content in soil, soil solutions, rocks, wet depositions, leaves and leaf litter.

All the experiments were performed using a range of methods such as ICP-MS, IC/ICP-MS, INAA, and XRF.

2. Materials and Methods

2.1 Plants experiments

2.1.1 Chemicals

All chemicals used in this experiments were in a purity of >99% and were dissolved in distilled water. Bromine solution was prepared using KBr (Sigma-Aldrich). Iodine solution was prepared using KI (Sigma-Aldrich). Phytagel (P8169, Sigma-Aldrich) was used as agar substitute.

2.1.2 Culture Setup

Hydroponic system was chosen as the preferred culture setup since it allows better inspection of plant health during the plant growth since the roots are not covered with soil. In addition, the use of hydroponic culture ease the after growth treatments and reduce contamination of other elements that may originate from the soil. Annual ryegrass (*Lolium multiflorum)* was chosen as the model plant due to its high yield potential and fast establishment.

The procedure was composed of 3 phases as shown in a flow chart (Fig. 11).

Phase 1: Seed holders were prepared by cutting the top 5 cm of 5 ml pipette tip and were autoclaved. *Lolium multiflorum* seeds were sterilized for 30 seconds in 70% Ethanol, 30 minute treatment in 1% sodium hypochlorite followed by a 5 times wash, 10 min in sterilized Millipore water. Phytagel was dissolved in nutrient solution (Table 6) to a concentration of 1.5% and the liquid was poured to a sterile box, the holders were putted in the liquid gel. After gelation, one sterile seed was placed in each holder above the gel and the closed box was transferred to a dark cooling room for 48 hours followed by a transfer to a growth chamber for 3 weeks (Sanyo, Gallencamp PLC at a photosynthetic active radiation (PAR) of 150 µmol·quantum/m^2s, 22°C/18°C day/night temperature and 60% RH, respectively. Light period was 16 hours).

Phase 2: After three weeks the seedlings including the holders were removed from the box and were fixed to a polystyrene plate which floated in a pot on a nutrient solution with an additional halogen supplement. Four seedlings were fixed to one plate. The final halogen concentrations for the experiments were: 0.05, 0.5, 5 mg/l while the control plant contained only the nutrient solution. Total pot volume was 3 liters. Each treatment was carried out in duplicate pots. The pots with the plants were transferred back to the same growth chamber.

Phase 3: The nutrient solutions with the supplemented halogens were replaced every week. The growth period was 7 weeks.

Table 6. Hydroponic nutrient solution.

Chemical component	Concentration (mg/l)
$Ca(NO_3)_2 \cdot 4H_2O$	951.7
$NH_4H_2PO_4$	60
KNO_3	610.6
$MgSO_4 \cdot 7H_2O$	490.3
NaOH	5
EDTA	33.2
$FeSO_4 \cdot 7H_2O$	24.8
H_3BO_3	0.6
$ZnSO_4 \cdot 7H_2O$	0.09
$CuSO_4 \cdot 5H_2O$	0.05
MoO_3	0.02
$Co(NO_3)_2 \cdot 6H_2O$	0.025
NH_4NO_3	0.007
$MnSO_4 \cdot H_2O$	0.35

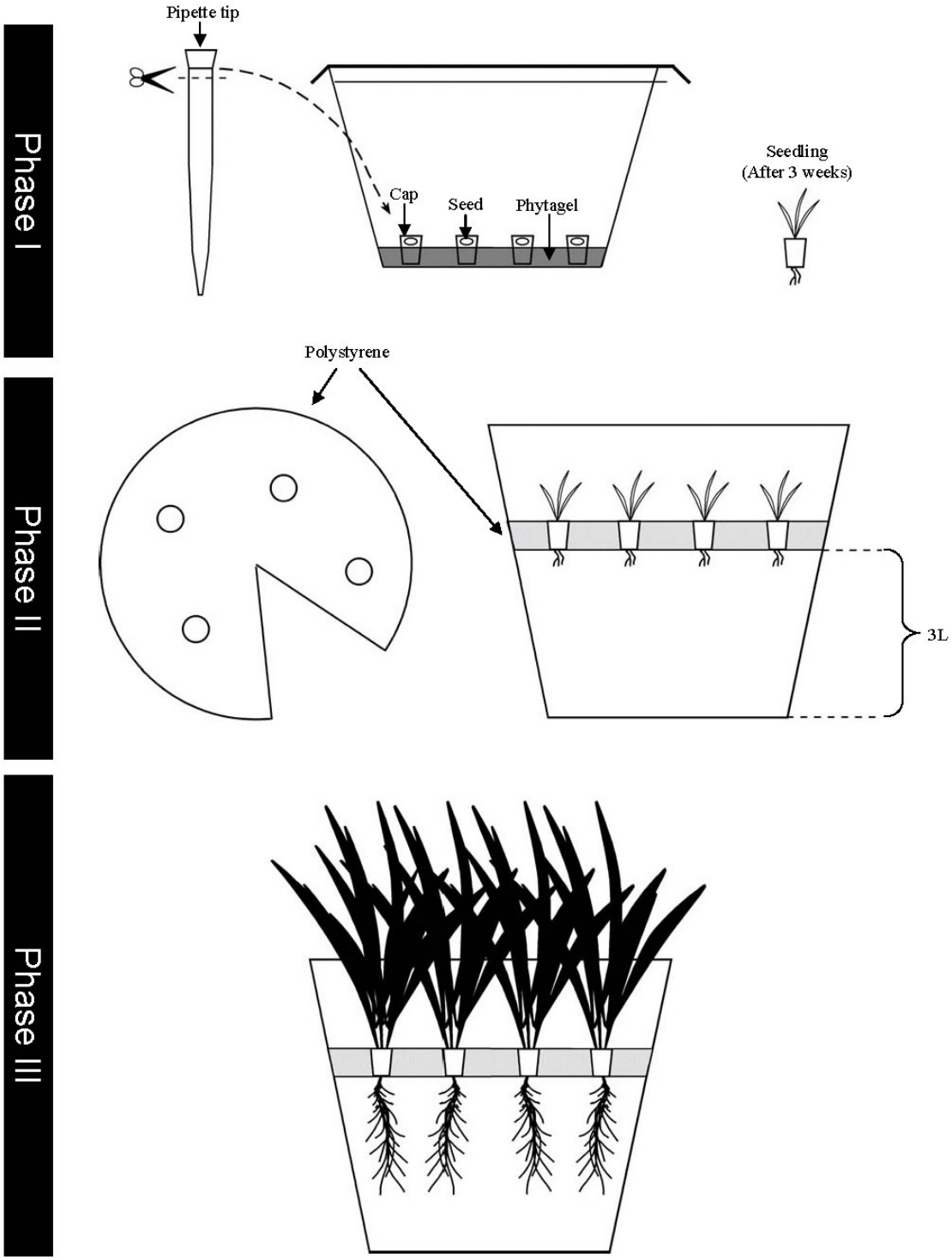

Fig. 11. Culture setup scheme.

2.2 *Lolium multiflorum* Decomposition experiment

2.2.1 Plant preparation, water and elements determination

The procedure was composed of 4 phases as shown in flow chart (Fig. 12).
Phase 1: Two plants for each pot were harvested resulting in 4 plants per treatment. The cultivated plants were washed twice with distilled water followed by two extra washes with Millipore water. Followed by measuring of their physical dimension parameters (total length, root length, leaf length).
Phase 2: The plants were dissected along their Y-axis into two parts.
Phase 3: One plant part was measured for water content by measuring the fresh weight and the dry weight after using a freeze dryer system. Total Br was determined using XRF as described elsewhere (Cheburkin and Shotyk, 1996). The sample weight ranged from 0.2-2g. Total Iodine was performed using INAA (Activation Laboratories Ltd., Ancaster, Canada), the sample weight ranged from 0.2-1 g. The other plant part was randomly sliced into large fragments and then transferred to a custom design decomposition apparatus.

2.2.2 Nomenclature of halogen enriched plant experiments

The two harvested plants from each pot pre treatment were decoded in the following form.
Bromine experiment: BconXY – control plant, Br1XY – 0.05 mg/l, Br2XY - 0.5 mg/l, Br3XY – 5 mg/l.
Iodine experiment: IconXY – control plant, I1XY – 0.05 mg/l, I2XY - 0.5 mg/l.
Halogen concentrations indicate the supplemented amount. XY – indicate the pot number/plant number.

2.2.3 Decomposition apparatus

The apparatus was a modified Erlenmeyer flask containing 30 ml Millipore water and the decomposing plant parts were retained in a net and hung above the water. The apparatus was shaken manually during the experiments in fixed intervals and all the leached solution was collected and replaced with new Millipore water. The leached fraction was filtered thorough 0.45 µm filter (Fisherbrand) and was measured for different elements and substances as described in section 2.2.5, 2.2.6 and 2.2.7. The decomposition period for the bromine enriched plants were

120 days while the iodine enriched plants were decomposed for 75 days. The decomposition process was performed in unsterile conditions.

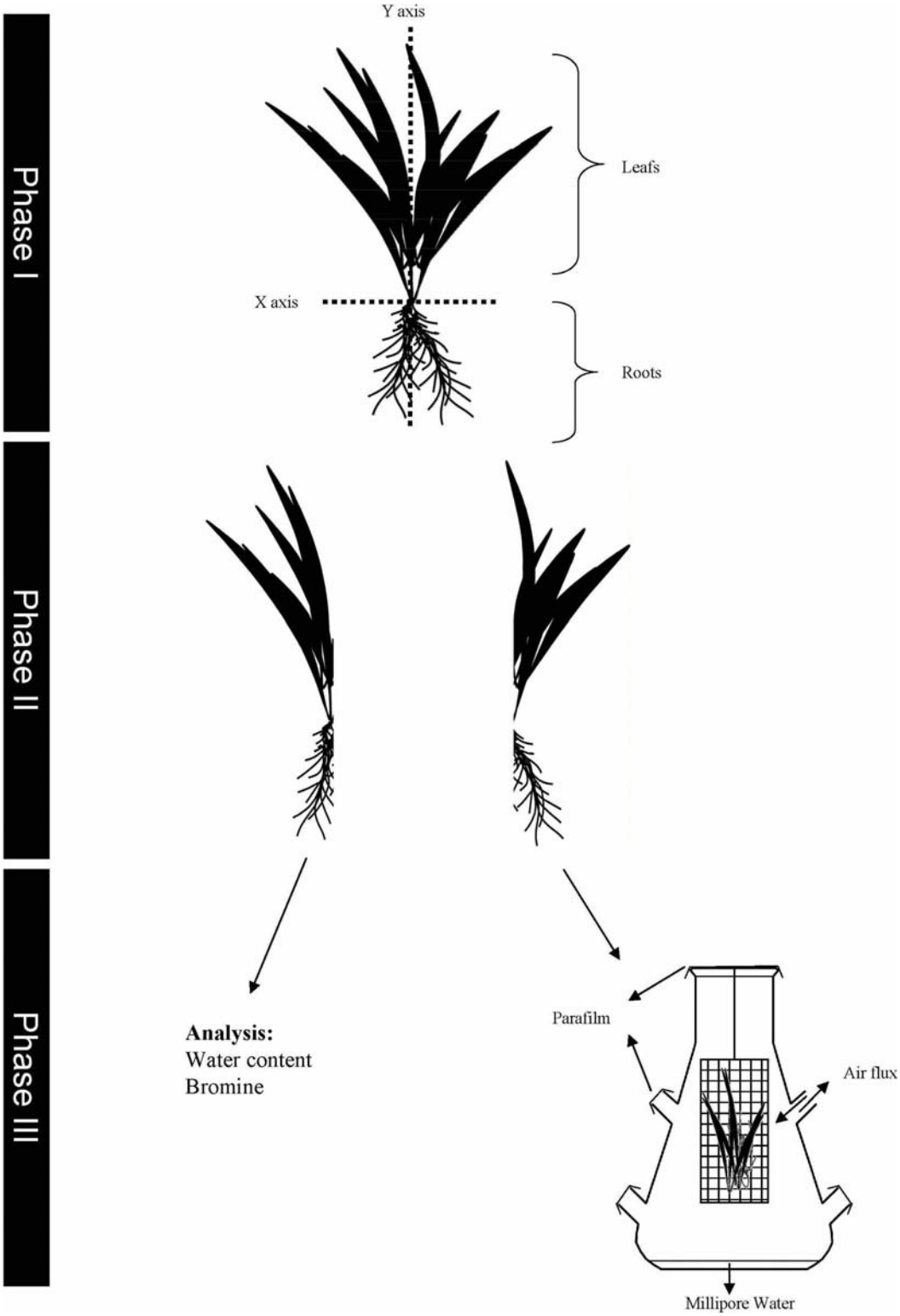

Fig. 12. Decomposition scheme.

2.2.4 Plant biomass treatments after decomposition

After decomposition period the plant remains were dried using a freeze dryer system and examined for various element content as described at section 2.2.1/phase 3.

2.2.5 Determination of total iodine and bromine and species in leached fraction

Total bromine and iodine in leached fraction were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer/Sciex Elan 6100 ICP-MS) using Rhenium as an internal standard. Analyses of bromine and iodine species were performed by ion chromatography inductively coupled plasma mass spectrometry (IC/ICP-MS) (Perkin-Elmer AS-90Plus, column Dionex IonPac AS16 (250x4mm), guard column AG16 (50x4mm), eluent was 35 mmol NaOH). All measurements of total bromine and iodine (indicative values) and bromide and iodide were in the range of the certified (indicative) values. Organobromine and organoiodine were calculated as the difference between total concentrations and the sum of the inorganic species concentrations.

2.2.6 Determination of dissolved organic carbon

Dissolved organic carbon (DOC) was determined using a Shimadzo TOC 5000 Analyzer.
Inorganic carbon standard was done by dissolving 0.35 g $NaHCO_3$ and 0.441 g Na_2CO_3 (water free) in 100 ml Millipore water resulting in a 1000 mg/l concentration.
Total carbon was done by dissolving 0.2125 g $C_8H_5KO_4$ in 100ml Millipore water resulting in a 1000 mg/l concentration.

2.2.7 Determination of nitrite, nitrate and sulphate

Total nitrite, nitrate, and sulphate were determinate by conductivity detector using Ion chromatography (Dionex DX-120, Dionex autosampler ASM-3, column Dionex IonPac AS14A (250x4mm) and guard column IonPac AG14A (50x4mm), eluent solution was 1mmol $NaHCO_3$ and 3.5mmol Na_2CO_3).

2.3. *Fagus Sylvatica* leaves Decomposition

2.3.1. Plant preparation, water and elements determination

The *Fagus Sylvatica* leaves were washed twice using Millipore water in order to remove leaves contamination and were separated to 5 groups. One group (68 g wet weight) was measured for water content by measuring the fresh weight and the dry weight after using a freeze dryer system and total Br was determined using XRF as described elsewhere (Cheburkin and Shotyk, 1996).

2.3.2. Decomposition apparatus

The procedure was described in section 2.2.3. The leaves were not cut before they retained in a net. The decomposition period was 92 days. The decomposition process was performed in unsterile conditions.

2.3.3. Plant biomass treatments after decomposition

The procedure was described in section 2.2.4.

2.3.4. Determination of total bromine in leached fraction

The procedure was described in section 2.2.5.

2.4. Soil experiment

2.4.1. Study area for halogen measurement

Soil, plants and leaf litter samples were collected from two different forest sites, Langer Kirschbaum (Sandstone site) and Leimen (Carbonate site), which are in the vicinity of the city Heidelberg, Germany. Annual precipitation is approximately 761mm for both sites. The two forests sites are dominated by Atlantic beech **(***Fagus Sylvatica*) trees. Parent rocks were formed during the Triassic period. Langer Kirschbaum bedrock was formed during the Buntsandstein (~Skyth epoch) while the formation of Leimen bedrock developed during the Muschelkalk (~Ladin/Anis epoch). The soil type at both of the sites is Cambisol.

2.4.2. Samples collection and preparation

Soil sampling was performed in January 2004. Soil profiles were excavated after removal of the leaf litter layers, which were also collected and separated to three layers based on the visible degree of decomposition. The soil profiles were partitioned into 12 sections. From soil surface (below leaf litter layers) and until a depth of 10 cm the sections were taken as follows: first section – 1 cm, second and third sections - every 2 cm. Deeper than 10 cm and until a depth of 55 cm the soil sections were sampled every 5cm. Fresh tree leaves and leaf litter sections were collected during the growth period from the same locations. The soil samples were air dried and ground prior to analysis.

Soil solutions were prepared by mixing 1g fresh soil with 10 ml Millipore water (18.3 mΩ), shake overnight, followed by a centrifugation (Heraeus Megafuge 1.0) for 10 min, 4000 rpm and then the supernatant was filtered through 0.45 μm filter (Fisherbrand). Rocks, rain and snow samples were collected from the study areas. The tree leaves and the litter were freeze dried and ground prior to analysis.

2.4.3. Determination of iodine and bromine species in soil, soil solution, rocks and plant material

Total bromine and iodine in soil solutions, snow and rain were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer/Sciex Elan 6100 ICP-MS) using Rhenium as an internal standard. Analyses of bromine and iodine species were performed by ion chromatography inductively coupled plasma mass spectrometry (IC/ICP-MS) (Perkin-Elmer AS-90Plus, column Dionex IonPac AS9HC (250x4mm) and guard column AS9GC (50x4mm), eluent 20mmol Na_2CO_3) according to the method of Sacher et al., 1999. The inorganic species measured were BrO_3^-, Br^-, IO_3^-, and I^-. 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. Organobromine and organoiodine were calculated as the difference between total concentrations and the sum of the inorganic species concentrations. Total bromine concentration in soil and plant material was performed using X-Ray Fluorescence Spectroscopy (XRF) as described elsewhere (Cheburkin and Shotyk, 1996). The sample weight ranged from 0.2-2 g. Iodine determination in soil and plant material samples was performed using Instrumental Neutron Activation Analysis (INAA) (Activation Laboratories Ltd., Ancaster, Canada), the sample weight ranged from 0.2-1 g.

2.4.4. Determination of pH, carbonate percentage, total carbon and dissolved organic carbon

Carbon was determined by means of a C/S-Analyzer (Leco SC-144DR) by burning 200 mg of sample. Carbonate measurement was done using carbonate bomb technique (Müller and Gastner, 1971). pH was measured after shaking a soil sample in Millipore water for 16h in a ratio of 1:10. The dissolved organic carbon (DOC) was measured according to the method described in section 2.2.6.

3. Results and discussion

3.1. Bromine experiment

3.1.1. Growth analysis

3.1.1.1. Physical dimension parameters

Physical dimension data (total length [cm], root length [cm], leaf length [cm] and root/leaf ratio) were analyzed for each plant and are presented in Table 7. One Way Analysis of Variance (ANOVA) of all the parameters indicate that the differences in the mean values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability. Due to that there is no statistically significant difference in the examined parameters. Bromine in the examined concentration did not influence growth.

Table 7. Plant physical dimensions after treatment with bromine.

Br. conc. in nutrient solution (mg/l)	Plant code	Total length (cm)	Root length (cm)	Leaf length (cm)	Root/Leaf ratio
Control	Bcon1A	118	49	69	0.71
	Bcon1B	80	29	51	0.57
	Bcon2A	112	45	67	0.67
	Bcon2B	92	38	54	0.70
	Average	101 ± 17.6	40.3 ± 8.77	60.3 ± 9.07	0.66 ± 0.07
0.05mg/l	Br11A	100	40	60	0.67
	Br11B	93	37	56	0.66
	Br12A	100	45	55	0.82
	Br12B	118	48	70	0.69
	Average	103 ± 10.7	42.5 ± 4.9	60.3 ± 6.85	0.71 ± 0.07
0.5mg/l	Br21A	122	46	76	0.61
	Br21B	107	35	72	0.49
	Br22A	112	45	67	0.67
	Br22B	100	32	68	0.47
	Average	110 ± 9.25	39.5 ± 7.0	70.8 ± 4.11	0.56 ± 0.1
5mg/l	Br31A	107	34	73	0.47
	Br31B	97	39	58	0.67
	Br32A	97	31	66	0.47
	Br32B	109	54	55	0.98
	Average	103 ± 6.4	39.5 ± 10.2	63 ± 8.1	0.65 ± 0.24

3.1.1.2. Bromine uptake by *Lolium multiflorum*

The plants were exposed to different bromine concentration in the growth solution (control, 0.05 mg/l, 0.5 mg/l and 5 mg/l). The uptake results are shown in Table 8. In the examined bromine concentration range no visual effect on growth was noticed during the growth phase, which indicates that this species might have a potential to grow in salinity areas. An average of 2.9 ± 0.55 mg/kg bromine was found in the control plant, one source for its presence is the low amount of bromine in the nutrient solution 9 ± 0.5 µg/l (n=5). The presence of bromine in the nutrient solution is related to the chemicals used although the chemical were in purity higher then 99%.

The average bromine concentration in herbage under natural condition range from 5 to 157 mg/kg, with a mean of 45 mg/kg (Wilkins, 1978). A concentration above 40 mg/kg can be related to pollution (Kabata-Pendias and Pendias, 2000). Consequently, the plants that were

cultivated with bromine concentration of 0.05 mg/l contain bromine concentrations which resemble to natural plants.

Table 8. Bromine uptake by *Lolium multiflorum*.

Bromine conc. in nutrient solution (mg/l)	Plant code	Br conc. in plant (mg/kg)
Control	Bcon1A	3.4
	Bcon1B	2.85
	Bcon2A	2.85
	Bcon2B	2.07
	Average	2.79 ± 0.55
0.05mg/l	Br11A	49.1
	Br11B	54.4
	Br12A	83.2
	Br12B	54.4
	Average	60.3 ± 15.5
0.5mg/l	Br21A	443
	Br21B	424
	Br22A	763
	Br22B	459
	Average	522 ± 161
5mg/l	Br31A	4938
	Br31B	4618
	Br32A	4265
	Br32B	5001
	Average	4705 ± 338

The bromine species in the plant are assumed to be inorganic and possibly stored in vacuoles. Vacuoles can function as a storage organelle and store many types of molecules, in particular substances that are potentially harmful if present in bulk in the cytoplasm. Examination of healthy *T. latifolia* and *P. australis* plant parts (leaf, stem, and root) using X-ray spectroscopy (XAS) revealed that bromine abounded as inorganic species. Furthermore, the absolute intensity of the bromine in these plants reveals that leaves have the highest Br- concentrations (Xu et al., 2004). Myneni (2002) showed that chlorine species in leaves are hydrated and H-bound Cl-. Although metal-complex –bound Cl and organochlorine might be present, their concentrations are below the XAS (X-ray spectroscopy) detection limit. Unlike chlorine, bromine in terrestrial wetland plants to exist in inorganic form (Xu et al., 2004).

3.1.1.3. Water content in plants

As described in the Materials and methods section (2.2.1) the plants were cut according to their Y-axis, one part of the plants was weighted before and after freeze drying in order to determine the amount of water. The water percentage results that are shown in Table 9 indicate a total average of 73 percent.

Table 9. Average plant water percentage.

Plant code	Total sample weight (g)		%Water
	Before freeze dryer	After freeze dryer	
BconXY	37.1 ± 17.7	9.6 ± 3.7	72.1 ± 5.6
Br1XY	36.2 ± 7.4	10.8 ± 0.4	69.4 ± 4.8
Br2 XY	40.5 ± 12.8	11 ± 0.88	71.3 ± 6.7
Br3 XY	37.4 ± 13.6	7.7 ± 3.7	79 ± 6
Average (All samples)	37.8 ± 12.0	9.8 ± 2.7	73 ± 6

3.1.1.4. CHNS content in bromine enriched plants

Plant nutrient which are taken up by the plant during the growth period, affects and indicates the plant physiology status. Diagnosis of nutrients is important in order to show if bromine was affecting the plant. Carbon, nitrogen, hydrogen and sulfur were analyzed, and the results are shown in Table 10. ANOVA analysis indicates that the carbon and sulfur differences are not great enough to exclude the possibility that the difference is due to random sampling variability.
Nitrogen is a critical component of proteins, which control the metabolic processes required for plant growth. It is also an integral part of the chlorophyll molecule and thus plays a key role in photosynthesis. An adequate supply of nitrogen is associated with vigorous vegetative growth and a plant's dark green color. Nitrogen data analysis indicates that there is a significant difference only between the plants that were grown in the concentration of 0.5 mg/l and 5 mg/l but not in-between the other treatments. The nitrogen deficiency observed in the 5 mg/l plants (group Br3) would require a larger data set and higher bromine concentration in order to determine if bromine affects the plant metabolism at the examined range.
Analysis of the hydrogen data shows that there is a significant difference between the control group and the 0.5 mg/l (Br2 group). The difference was also observed between the control group and the 5 mg/l (Br3 group). Hydrogen is a fundamental building block. The deficiency observed in the 0.5 and 5 mg/l treatments plants may indicate osmotic and ionic stresses as a result of the

high level of bromine. Some hydrogen related mechanisms are associated to stress, one of them is an increase in the activities of the H^+-pumps. Another mechanism possibly involve is Na^+/H^+ antiporter (exchanger) which catalyses the exchange of Na^+ for H^+ across membranes (Fukuda et al., 2004). Further investigations are necessary in order to find if these mechanisms are affected by the high bromine concentration in plant and in growth solution.

Table 10. CHNS content in bromine enriched plants.

Plant code	Element			
	C (%)	H (%)	N (%)	S (mg/kg)
Bcon1A	37.3	5.63	5.23	4606
Bcon1B	36.6	5.52	5.19	4587
Bcon2A	35.5	5.13	5.57	4110
Bcon2B	35.6	4.96	5.56	6162
Average	36.3 ± 0.8	5.31 ± 0.32	5.39 ± 0.21	4866 ± 893
Br11A	36.4	4.82	5.06	4155
Br11B	35.8	4.58	5.41	4917
Br12A	36	5.55	5.43	4123
Br12B	35.3	4.27	5.66	5721
Average	35.9 ± 0.5	4.81 ± 0.55	5.38 ± 0.25	4729 ± 756
Br21A	35.3	4.27	5.86	4348
Br21B	36	4.44	5.43	4312
Br22A	35.3	4.36	5.95	4728
Br22B	37.3	4.5	5.29	5786
Average	36 ± 0.94	4.39 ± 0.1	5.63 ± 0.32	4793 ± 687
Br31A	37.2	4.36	5.06	4116
Br31B	36.5	4.34	5	3950
Br32A	36.3	4.41	5.3	4118
Br32B	37.1	4.4	4.93	5469
Average	36.8 ± 0.4	4.38 ± 0.03	5.07 ± 0.16	4413 ± 708
P	0.31	0.004	0.045	0.46

*P<0.05 significant

3.1.1.5. Overall bromine concentration in the plants

The amount of bromine in plants was calculated by using equation 1. The biomass percentage (100%-water percentage) was multiplied with the total wet weight of the plant resulting the calculated dry weight (CDW). The CDW was again multiplied by bromine concentration

resulting the calculated bromine content for the entire plant (CBC). The results for each plant are shown in Table 11. The calculation is assuming that both parts of the plants contain the same water content and the similar distribution of bromine concentration.

Equation 1: Calculated bromine content in plant

$$CDW\ (\text{Calculated dry weight}) = \left(1 - \frac{\%Water}{100}\right) \cdot TW\ (\text{Total weight})$$

$$CBC\ (\text{Calculated Br content}) = CDW \cdot Br\ conc.$$

Table 11. Calculated bromine content in bromine enriched plants.

Plant code	%Water	TW-Total weight (g)	Br conc. (µg/g)	CDW-Calculated dry weight (g)	CBC- Calculated Br content (µg)*
Bcon1A	76.7	79.6	3.4	18.5	62.9
Bcon1B	64.4	22.8	2.85	8.11	23.1
Bcon2A	71.6	59.2	2.85	16.8	47.9
Bcon2B	75.7	64.1	2.07	15.6	32.3
Average	72.1 ± 5.6	56.4 ± 24.1	2.79 ± 0.55	14.7 ± 4.6	41.6 ± 17.5
Br11A	65.6	77.7	49.1	26.7	1311
Br11B	67.4	47.9	54.4	15.6	851
Br12A	76.5	70.9	83.2	16.6	1384
Br12B	68.2	48.1	54.4	15.3	834
Average	69.4 ± 4.8	61.1 ± 15.4	60.3 ± 15.5	18.6 ± 5.46	1095 ± 293
Br21A	76.1	81.6	443	19.5	8637
Br21B	78.2	84.3	424	18.4	7787
Br22A	66.4	49.4	763	16.6	12660
Br22B	64.7	59.5	459	21.0	9631
Average	71.3 ± 6.7	69±17	522 ± 161	18.9 ± 1.85	9678 ± 2115
Br31A	75.9	78.1	4938	18.9	92983
Br31B	87.8	58.6	4618	7.14	32993
Br32A	74.9	43.3	4265	10.9	46368
Br32B	77.5	77.4	5001	17.4	87127
Average	79 ± 6	64.4 ± 16.7	4706 ± 338	13.6±5.5	64896 ± 29723

*Bromine amount calculation for the entire plant and based on dry weight

3.1.1.6. Bromine concentration in decomposed plant part

The same calculation and assumption as in section 3.1.1.5 were applied. Though, the calculation is based on the wet weight of the decomposed part. The calculation is shown in Table 12.

Table 12. Calculated bromine content in plant decomposed parts.

Plant code	%Water	DW-Decompose weight (g)	Br conc. (µg/g)	CDW-Cal. dry weight (g)	DCBC-Decomp. Cal. Br content (µg)
Bcon1A	76.7	29.7	3.4	6.92	23.5
Bcon1B	64.4	11.3	2.85	4.02	11.5
Bcon2A	71.6	19.8	2.85	5.62	16.0
Bcon2B	75.7	16.7	2.07	4.06	8.4
Average.	72.1 ± 5.6	19.4 ± 7.7	2.79 ± 0.55	5.16 ± 1.39	14.8 ± 6.6
Br11A	65.6	45.2	49.1	15.5	762
Br11B	67.4	15.5	54.4	5.06	275
Br12A	76.5	23.5	83.2	5.53	460
Br12B	68.2	15.5	54.4	4.93	269
Average	69.4 ± 4.8	24±14	60.3 ± 15.5	7.8 ± 5.2	441 ± 231
Br21A	76.1	34.4	443	8.23	3646
Br21B	78.2	29.0	424	6.33	2684
Br22A	66.5	19.0	763	6.38	4869
Br22B	64.7	30.4	459	10.7	4917
Average	71.3 ± 6.7	28.2 ± 6.6	522 ± 161	7.92 ± 2.07	4029 ±1073
Br31A	75.9	29.9	4938	7.21	35608
Br31B	87.8	20.7	4618	2.53	11668
Br32A	74.9	25.3	4265	6.35	27076
Br32B	77.5	32.0	5001	7.20	36019
Average	79 ± 6	27 ± 5	4705 ± 338	5.82 ± 2.23	27593 ± 11389

3.1.2. Decomposition of bromine enriched plants

3.1.2.1. Decomposition of control plants

The first plants to be examined were the control plants that were not enriched with bromine during the growth period. The data of the first control plant is shown in Fig. 13. The graphs are presented in the following order: graph 13A shows the concentration of bromine in the leached fraction versus decomposition time, graph 13B shows the organobromine concentration versus the total bromine concentration in the leached fraction and graph 13C shows the percentage of

organobromine and inorganic bromine from the total bromine in the leached fraction. The figure structure will be repetitive during the whole section.

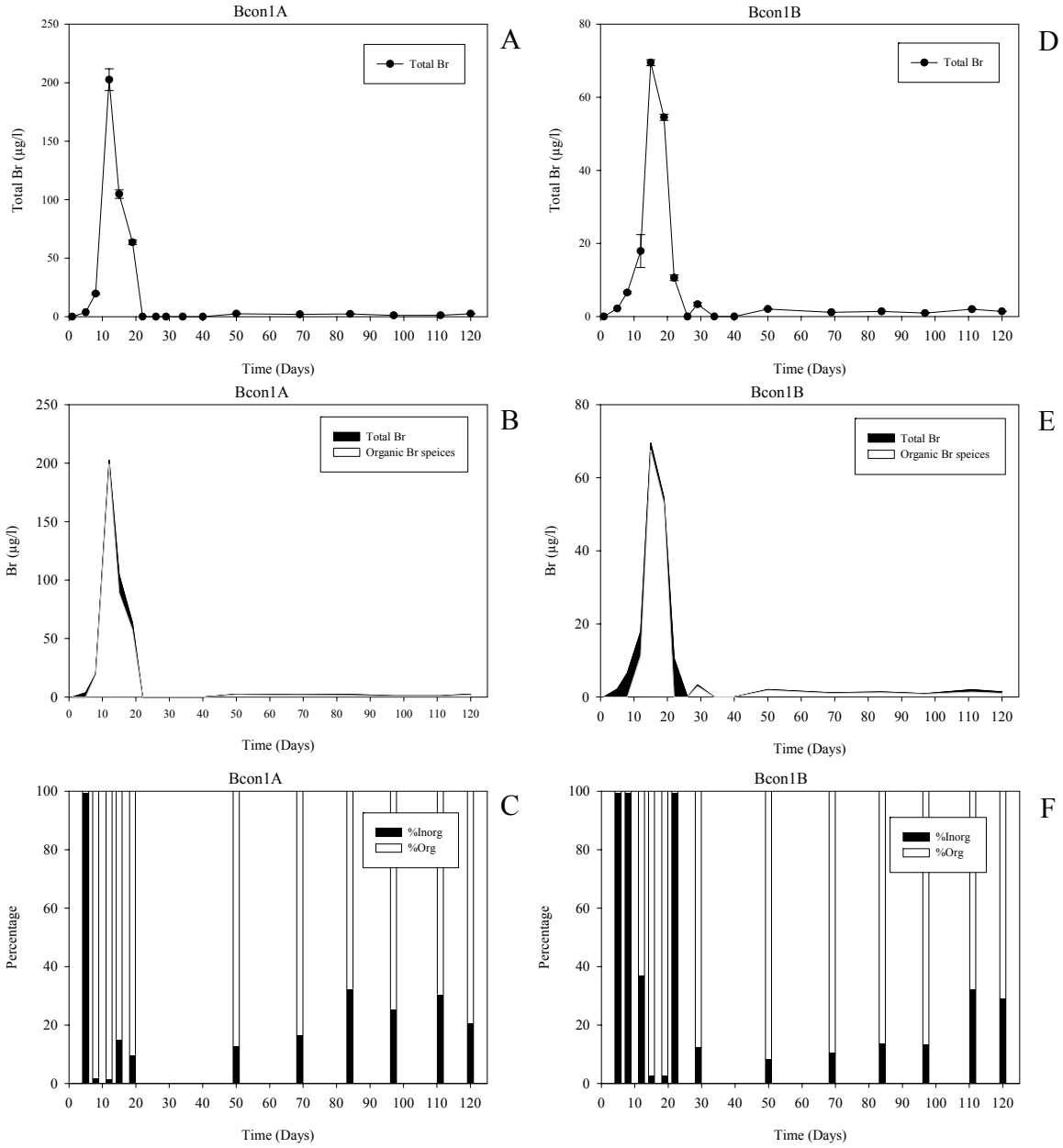

Fig. 13. Bromine concentration and speciation of control plants leached fraction during 120 days of decomposition.

From the results of the first plant shown in graph 13A we can noticed that the maximum bromine leached to the solution occurred at day 12 (202.5 ± 9.3 µg/l), whereas at day 22 and until day 40 no bromine was leached. The speciation data shown in graph 12B, C reveal that during the first week all the bromine was in inorganic form. From day 8 on the organobromine species are the dominant species (77 ± 17.5 µg/l).

The decomposition result of the second control plant (graph 13D, E, F) shows a similar a pattern. Maximum bromine is leached within 15 days (69.5 ± 0.84 µg/l). Compared to the first control

plant the maximum bromine concentration and the sum of all the bromine leached were lower due to a different initial bromine amount in the plant decomposed part (29.7 g, 11.32 g respectively). Speciation distributions were similar, during the first eight days of the experiments all the bromine was in inorganic form followed by a transition to organobromine species (concentration of 71.5 ± 27.7 μg/l until the termination of the experiment).

The third control plant (graph 14A, B, C) exhibits the same pattern in all parameters examined. The maximum bromine leached occurs at day 15 (104 ± 3.4 μg/l). Inorganic bromine was the only species in the first eight days and in the rest of the days (except day 29) organobromine was the dominant species 79 ± 12.2%.

The fourth control plant result exhibit a minor difference in the total bromine leached. Two peaks are noticed in the decomposition pattern and are probably the effect of the plant fragmenting applied in the beginning of the experiments (plant cutting). The cutting of the plant at the beginning of the experiment was in order to increase the plant surface to attack by microorganisms, which in the fourth plant results two breach events. The events occurred in day 15 and day 22.

Examination of the all control results reveals that the major leaching events occur within three weeks from the beginning of the experiments. The events are mainly caused by the destruction of the cell wall and leaching of the plant cell content. Inorganic species are the dominant fraction at the beginning of the decomposition process possibly due to the inorganic bromine stored in the plant as mentioned by Xu et al., (2004). The following transition to an organic fraction might indicate the establishment of microorganism communities in the solution, resulting in the creation of organobromine. The organobromines can also be formed by chemical reactions with secondary compounds. The microorganism establishment is a function of time which is required to create a stable communities and a low inorganic bromine concentration.

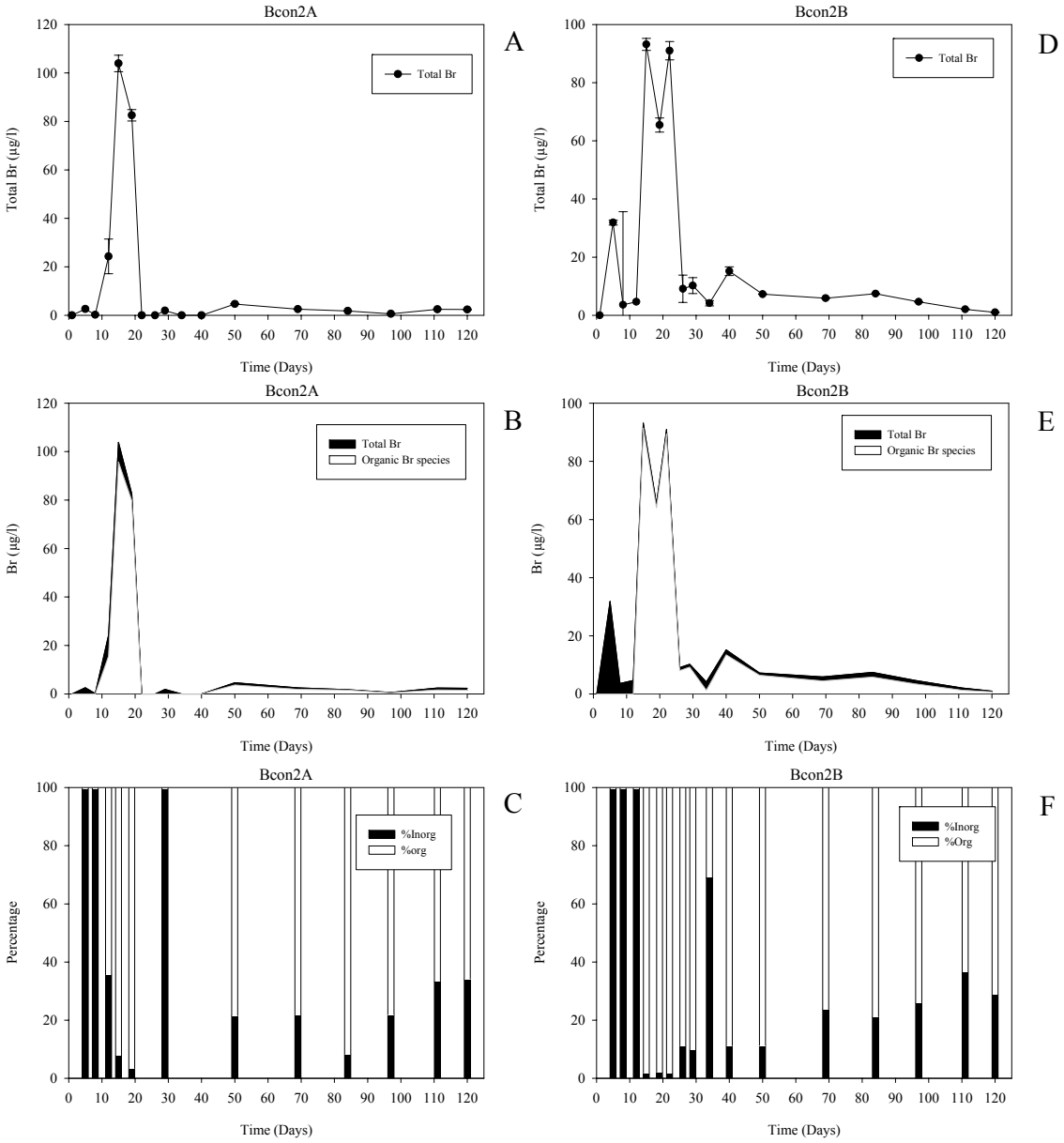

Fig. 14. Bromine concentration and speciation of control plants leached fraction during 120 days of decomposition.

3.1.2.2. Decomposition of plants grown with 0.05 mg/l bromine

Decomposition results of the plants grown with 0.05mg/l supplemented bromine are shown in both Fig. 15 and Fig. 16. The leaching processes are similar to the process that occurred in the control plants. Maximum release occurred at day 12 of the experiments (graph 15A, D and graph 16A, D). In graph 15A a higher rate of bromine release is occurring, compared to the other results described. This pattern again is related to the fragmentation effect, which enhances the microorganisms' attack on the plant debris, resulting in a high bromine release. The speciation results reveal again that in the first twelve days all the bromine is inorganic, followed by an

appearance of organobromine species. Maximum release of bromine was observed in plant Br12A where the peak release was 1042 µg/l.

The different patterns of organobromine percentage during the entire decomposition time in each plant are assumed to be related to the different amount of bromine released and to the performance of microorganism under bromine presence. Bromine in high concentration can be a stressful ion and might affect the microorganism osmotic regulation mechanisms, by that only the fitted microorganisms which grow with this interference will thrive in the system. The diversity of microbial communities generally decreases in response to environmental stress and disturbances, resulting that the population that becomes dominant within the disturbances communities possess nutritional characteristics directly related to the disturbance (Atlas et al., 1991).

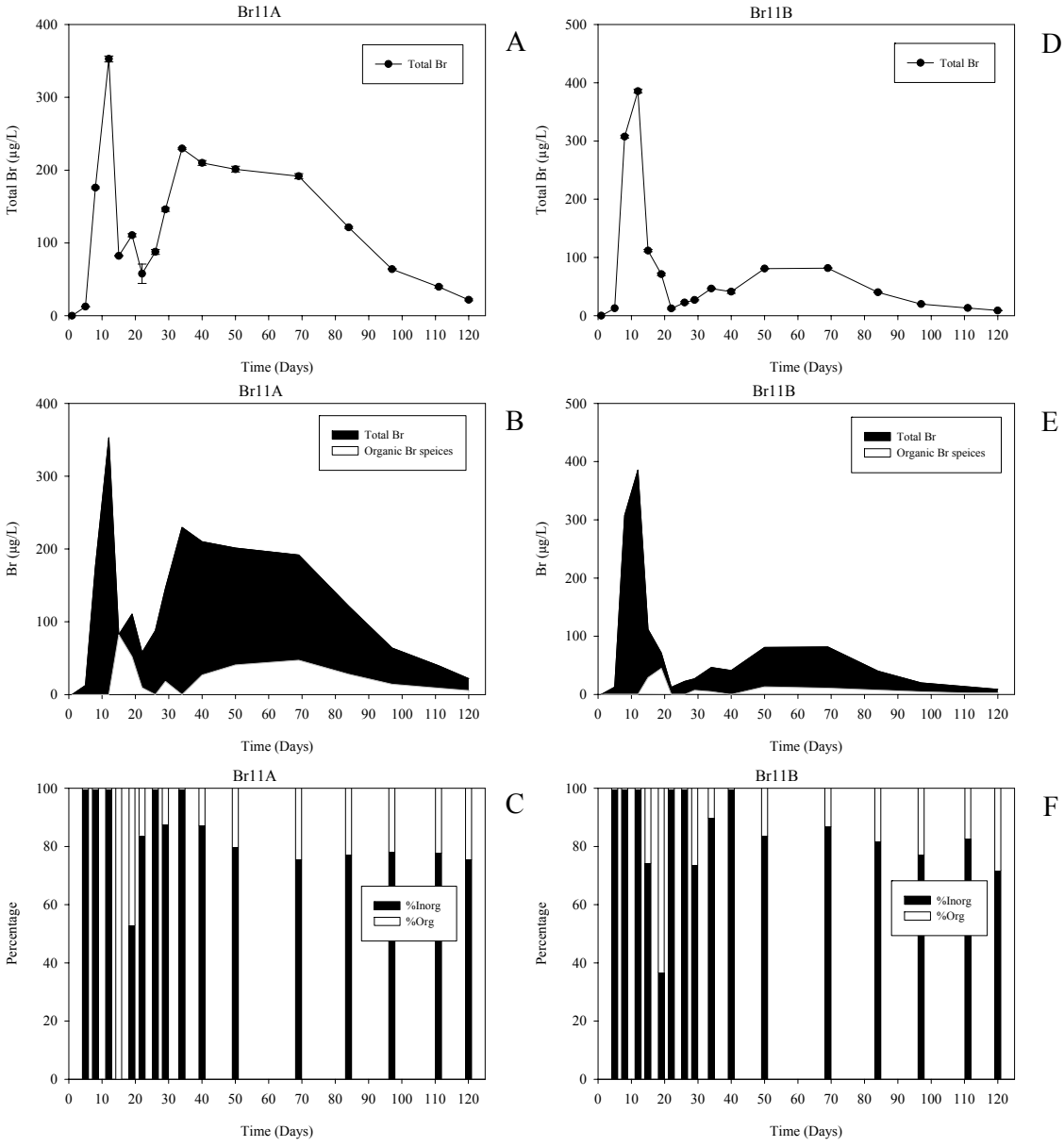

Fig. 15. Bromine concentration and speciation of 0.05 mg/l plants leached fraction during 120 days of decomposition.

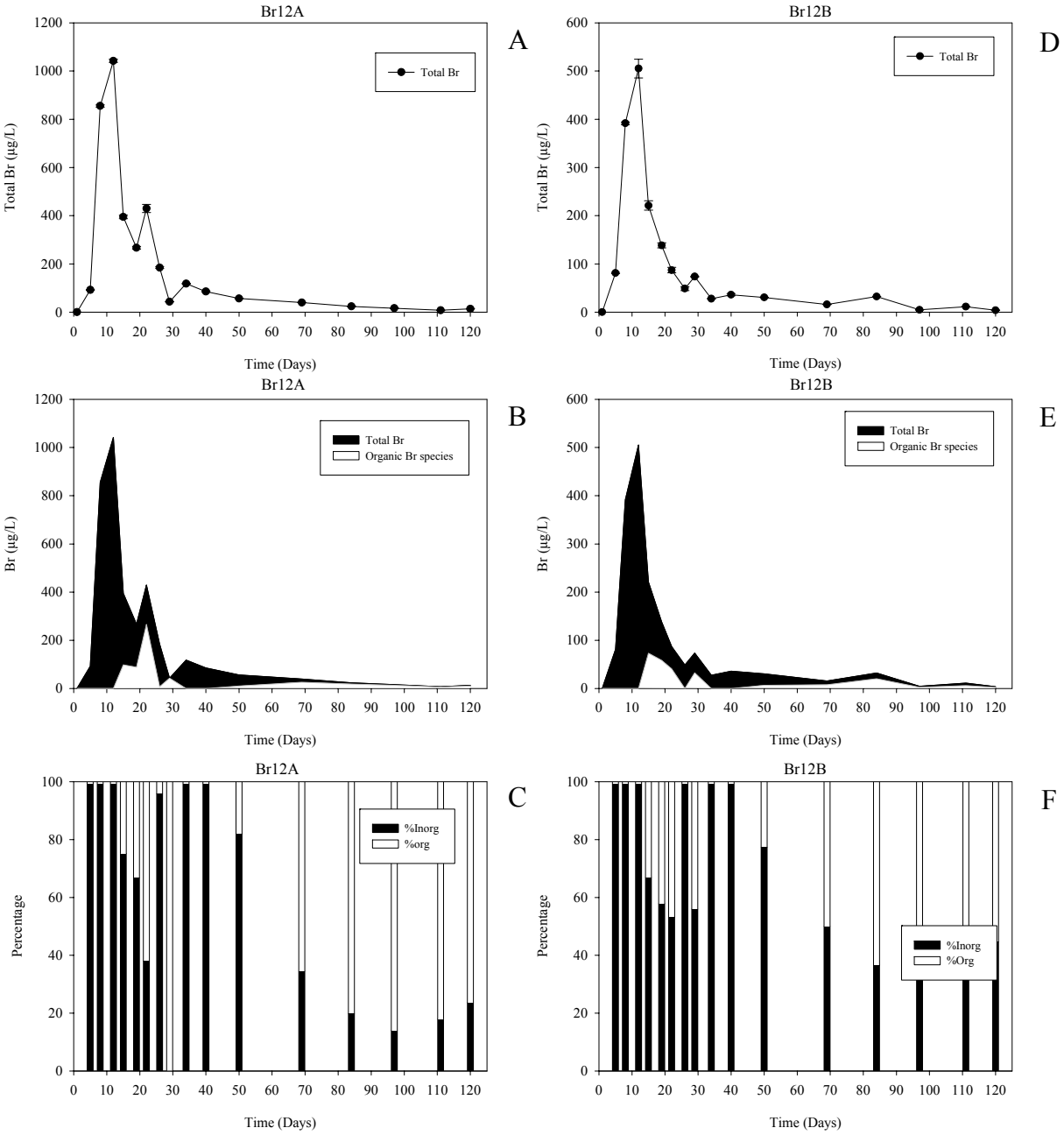

Fig. 16. Bromine concentration and speciation of 0.05 mg/l plants leached fraction during 120 days of decomposition.

3.1.2.3. Decomposition of plants grown with 0.5 mg/l bromine

The leaching pattern results shown in graph 17A, B and graph 18A, B are similar, once again showing fragmentation effects (graph 17D, E). The bromine released is higher compared to the other plants examined until now, maximum release of bromine was noticed in plant Br22A where the peak release was ~12 mg/l. Inorganic bromine are the dominant species in the first forty days of the experiment. Around day 50 a sudden increase of organobromine species occur

which might indicate a transition in the microorganism communities due to the decrease in the bromine concentration.

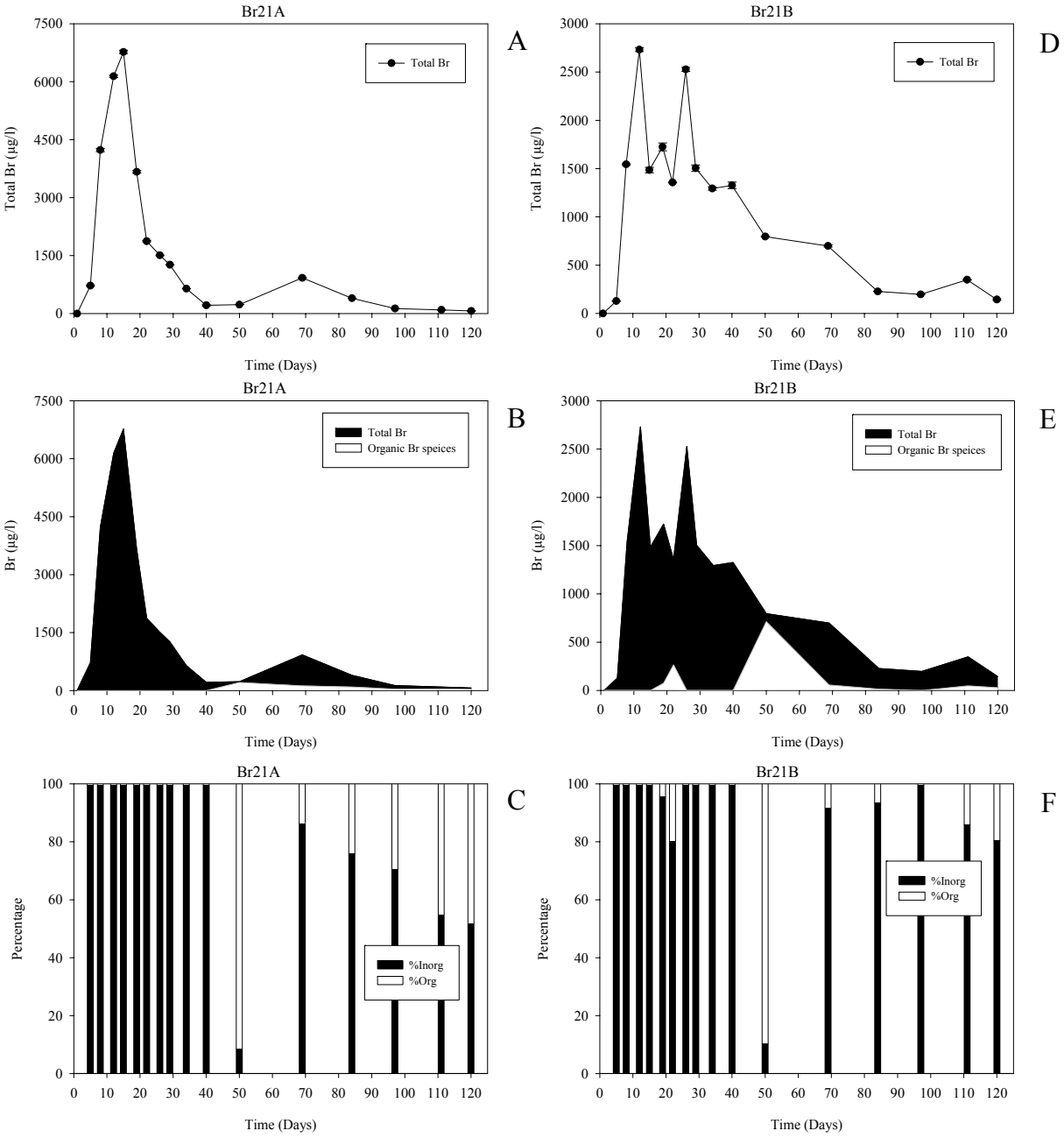

Fig. 17. Bromine concentration and speciation of 0.5 mg/l plants leached fraction during 120 days of decomposition.

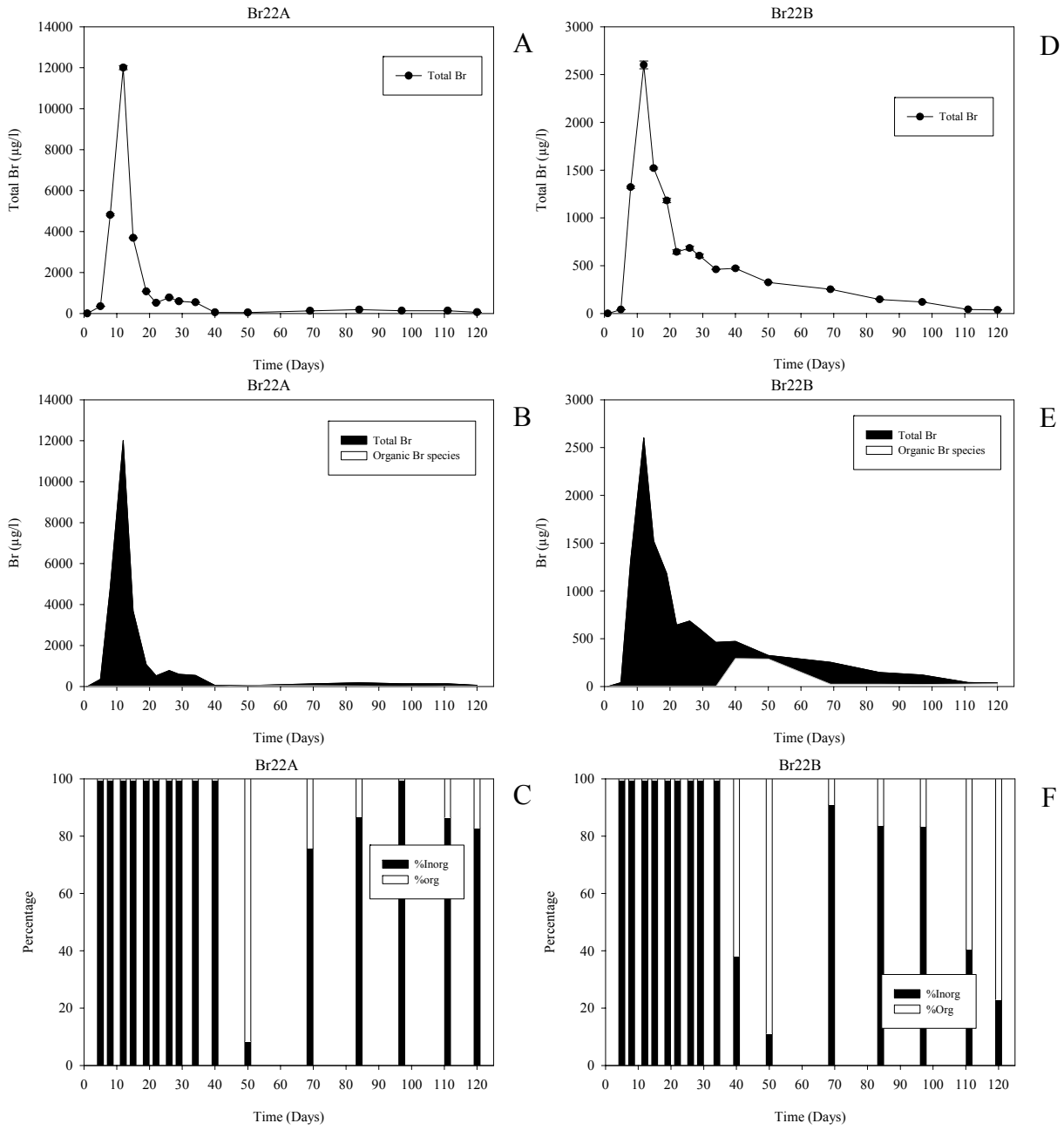

Fig. 18. Bromine concentration and speciation of 0.5 mg/l plants leached fraction during 120 days of decomposition.

3.1.2.4. Decomposition of plants grown with 5 mg/l bromine

The decomposition results pattern (shown in Fig. 19 and 20) are similar to the previous ones and as the concentration increases the differences between the samples are less pronounced due to the toxic bromine concentrations effect on the organisms in the decomposition vessel. No organobromine is present in the first forty days (in one samples it occurs at day 34) followed by a sudden increase in organobromine at day 50. The fraction of organobromine species after day

50 is below 60% (average result) and is associated again with the presence of microorganisms and the establishment of communities.

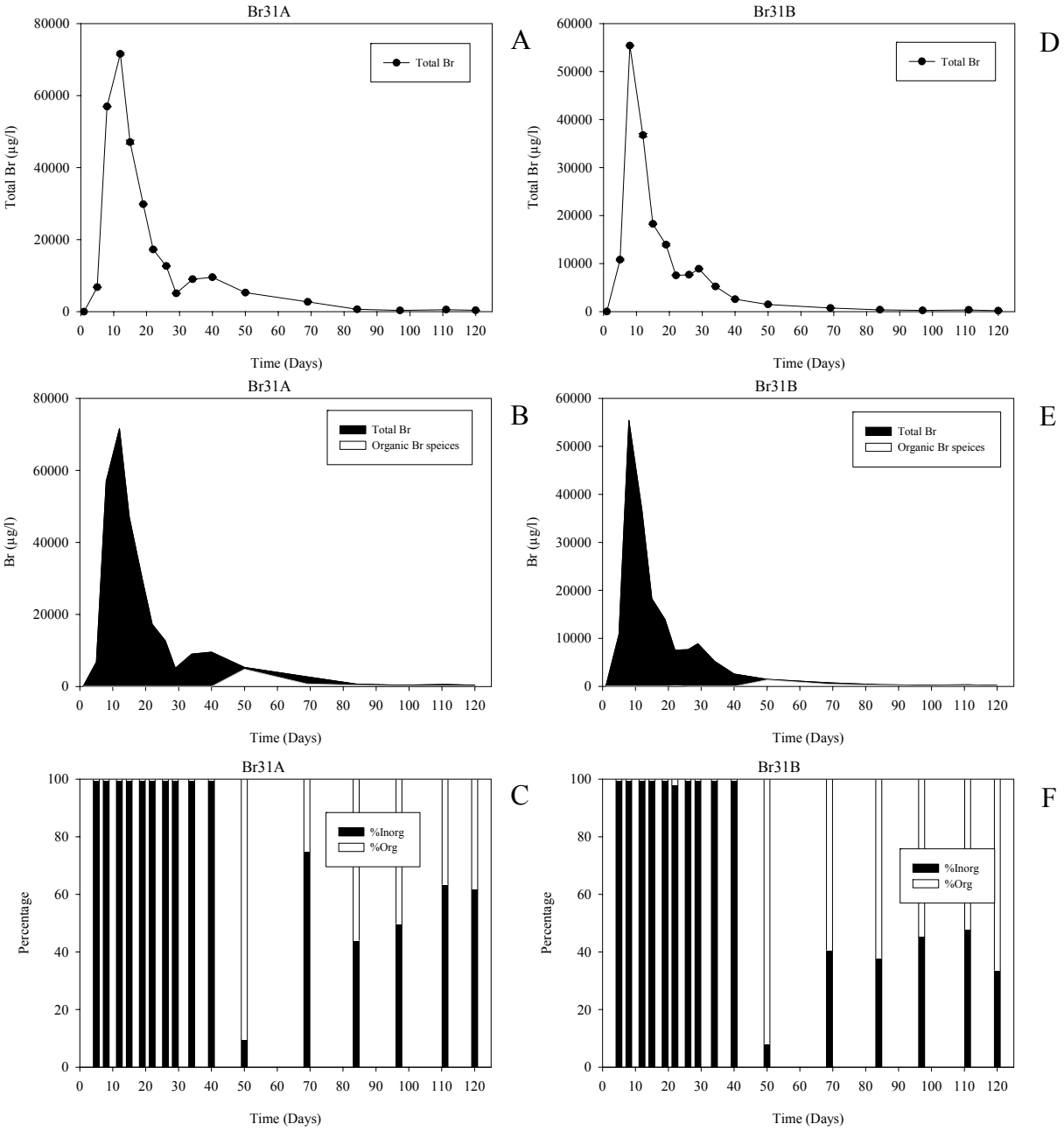

Fig. 19. Bromine concentration and speciation of 5 mg/l plants leached fraction during 120 days of decomposition.

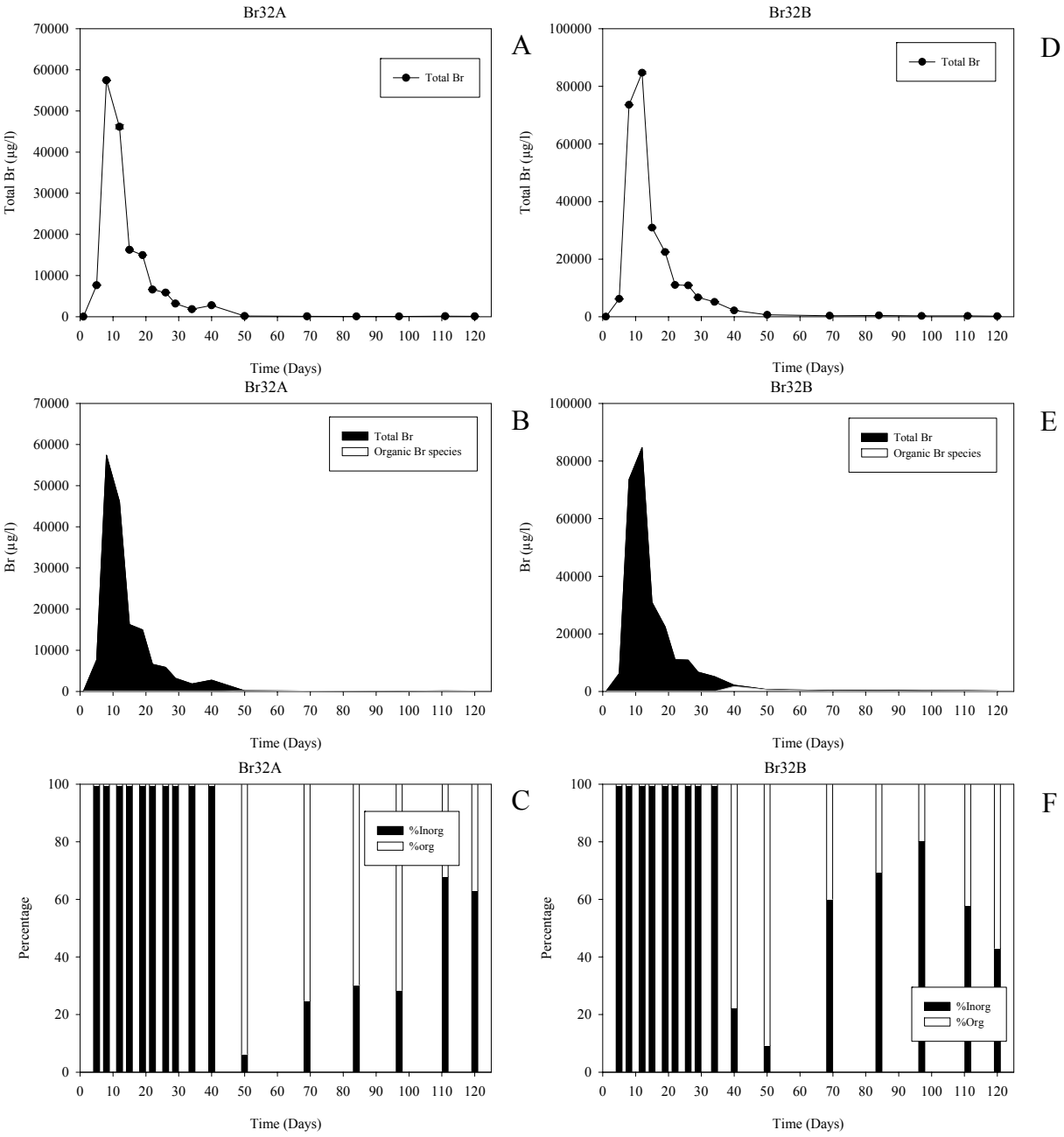

Fig. 20. Bromine concentration and speciation of 5 mg/l plants leached fraction during 120 days of decomposition.

3.1.2.5. Bromine enriched plants decomposition summary

A summary of the results reveals that the average bromine releases form the plants were different due to different initial bromine concentrations although the release patterns were the same. The presence of inorganic bromine in the beginning of the decomposition is related to the bromine storage form in the plant (inorganic species). The appearance of organobromine was detected when the concentration of total bromine in the leached solution was decreasing. The decrease of

bromine allows the establishment of microorganisms with a higher diversity which may produce organobromine. Another option for the creation of organobromine is by a chemical reaction of bromine with microorganisms' metabolites or other secondary compounds.

3.1.2.6. Bromine mass balance

Bromine in the stratosphere is 50–60 times more effective than chlorine (per-atom) in depleting ozone and can be emitted from versatile sources. A compilation of a bromine mass balance in a decomposition system was one of the aims of this work in order to understand if this biological process contributes to the global budget (bromine volatile species release during decomposition) and if it is environmentally significant. In order to perform this calculation several calculations have been applied and are described in Equations 2-4.

Equation 2: Percentage of leached bromine

$$\mathrm{Br}_{\mathrm{leached}}\ (\mu g) = \sum(\text{Volume of leached fraction} \cdot \text{Total bromine in leached fraction})$$

$$\%\ \text{Bromine leached} = \frac{\mathrm{Br}_{\mathrm{leached}}}{DCBC} \cdot 100$$

*DCBC-Decomp. Cal. Br content (µg)

The amount of bromine remains in the plant was calculated as shown in equation 3.

Equation 3: Percentage of bromine that remains in the plant

$$\mathrm{Br}_{\mathrm{remain}}\ (\mu g) = \text{Bromine concentration in debris} \cdot \text{Plant detritus dry weight}$$

$$\%\ \text{Bromine remain in plant} = \frac{\mathrm{Br}_{\mathrm{remain}}}{DCBC} \cdot 100$$

The amount of bromine volatilized during the decomposition is the subtraction of both phases calculated from 100% as shown in equation 4.

Equation 4: Percentage of bromine volatile during decomposition

$$\%\ \text{Volatile bromine} = 100\% - \mathrm{Br}_{\mathrm{remain}} - \mathrm{Br}_{\mathrm{leached}}$$

The results for each bromine treatment are presented in Fig. 21.

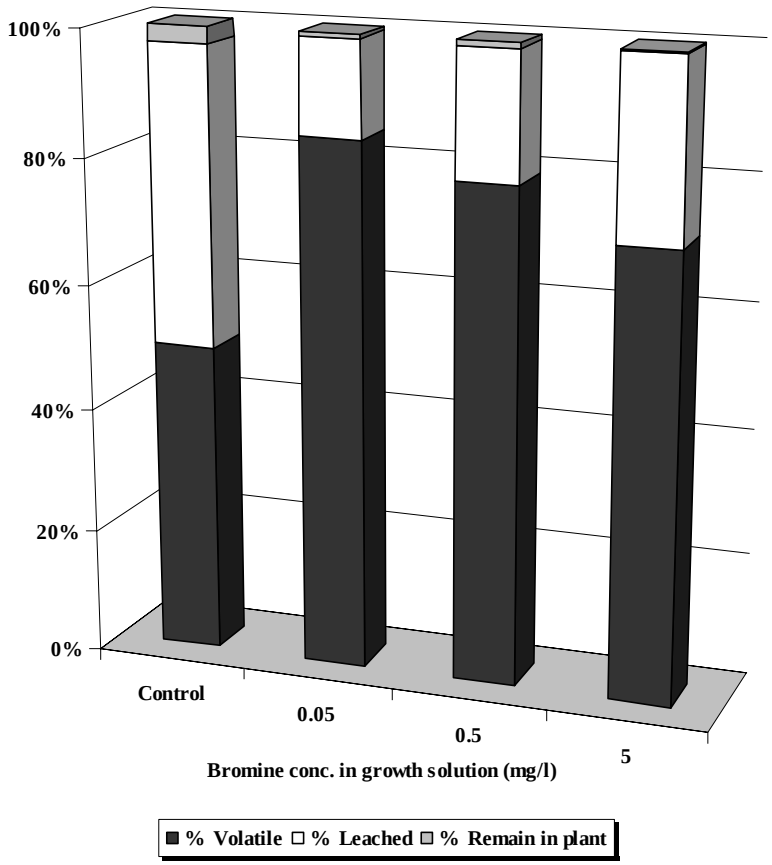

Fig. 21. Bromine mass balance.

The mass balance of bromine (Fig. 21) reveals that in the control plants the bromine amount which is leached and fraction that volatilized are almost identical. The amount remaining in the plants after decomposition is low. As the bromine concentration in the growth solution increased (treatments 0.05, 0.5, 5 mg/l) the amounts which were leached during decomposition increased, while the volatile amounts behave the other way around. The bromine amount remaining in the decomposed plants are also low.

Unlike the species behavior in the leached solution, which was described earlier, the volatile bromine fraction was not inspected for its compounds. A possible volatile compound is methyl bromide (MeBr, CH_3Br), a molecule with low boiling point (3.6°C, at 1Atm.) and a high vapor pressure. It is known that microorganisms release CH_3Br to the environment (Scarratt and Moore, 1996).

CH_3Br is the largest carrier of bromide to the atmosphere and is involved in stratospheric ozone depletion (Rhew et al., 2000). Sources for only 60% of the sinks for methyl bromide could be accounted for, and it seems that the missing sources of this gas can be terrestrial (Butler, 2000).

Unlike other organohalogens (e.g. CFCs), atmospheric MeBr is not entirely emitted by human activities. Atmospheric CH_3Br has abundant natural and anthropogenic sources. Also, its sinks are not only reactions with the atmosphere, but also interaction with the oceans and land. Various

processes involving plants indicate that they can serve as a sink or source for methyl bromide, but the processes are not well quantified globally (Jeffers et al., 1998; Lee-Taylor and Holland, 2000). The results shown in the section indicate that up to 84% of the initial bromine in the plant can be volatilized. The work of Lee-Taylor and Holland, (2000) suggests that the CH_3Br flux of 0.5-5.2 kT/yr can be due to litter decomposition. Redeker et al., (2004a) showed that ectomycorrhizal fungi can also emit methyl halides but it varies among species. As a result a global extrapolation is difficult to perform and depends on many variables such as different bromine content in plant species and different decomposition rates. Nevertheless, litter decomposition can be a valid source and/or sink that might help to balance the global budget. Furthermore, the results of this experiment indicate the role of the terrestrial environment in the current budget might be underestimated.

3.1.2.7. TOC results

Organic carbon release from plants during decomposition is known in various ecosystems (Swift et al., 1979) and includes versatile compounds. Some organic molecules have the possibility to bind halogens and by that creating organohalogens. TOC (total organic carbon) percentage was calculated by its percentage from total carbon, results of all the treatments were plotted versus time as shown in Fig. 22. The behavior of the TOC percentage in all experiments was similar regardless to the different bromine gradient in the treatments growth solution. The TOC data can be correlated to a simple equation which reveals that the relative amounts of TOC in the beginning of the experiment are low due to the fact that the decomposition does not occur instantly, but at day 5 it is already at a level of 50% ± 10 followed by a study increase through the entire examined time. The results indicate that there is a constant flow of organic matter during the decomposition process via leaching.

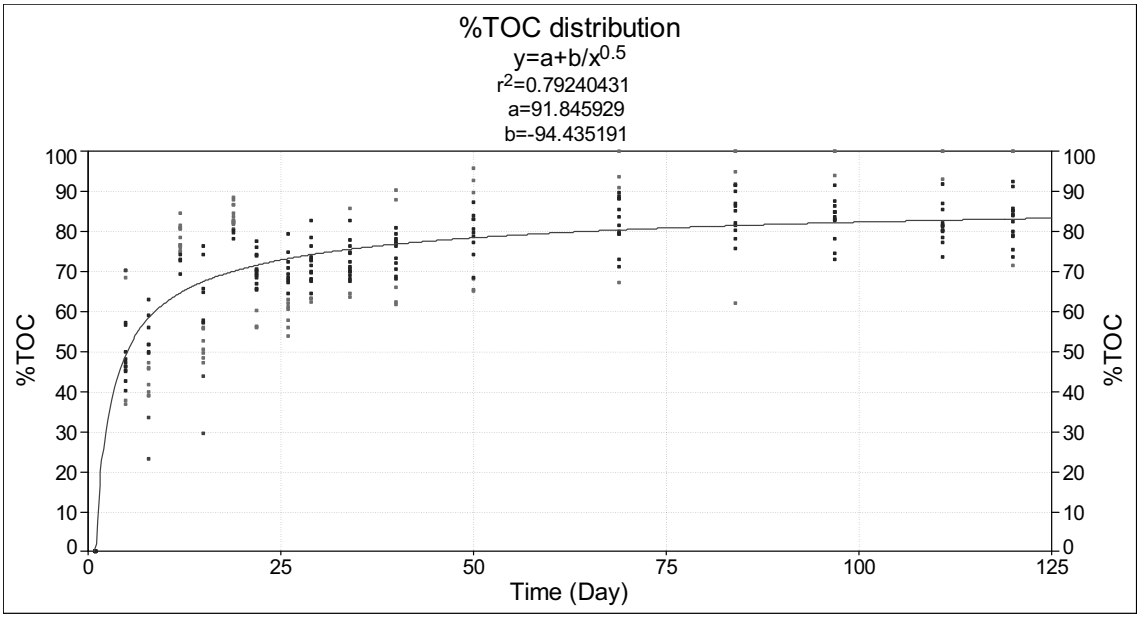

Fig. 22. Behavior of TOC (percentage) during decomposition process.

Unlike the TOC percentage plot the IC (inorganic carbon) percentage versus time (Fig. 23) can not be correlated easily. An analysis of the data discloses that the IC percentage variations within the first weeks of decomposition are high. The variation may be related to the lack of established microorganism communities and reflect the ambient CO_2 level in every vessel. As the decomposition proceeds the bacterial respiration and the CO_2 diffusion are getting less irregular which will result in a steady correlation line.

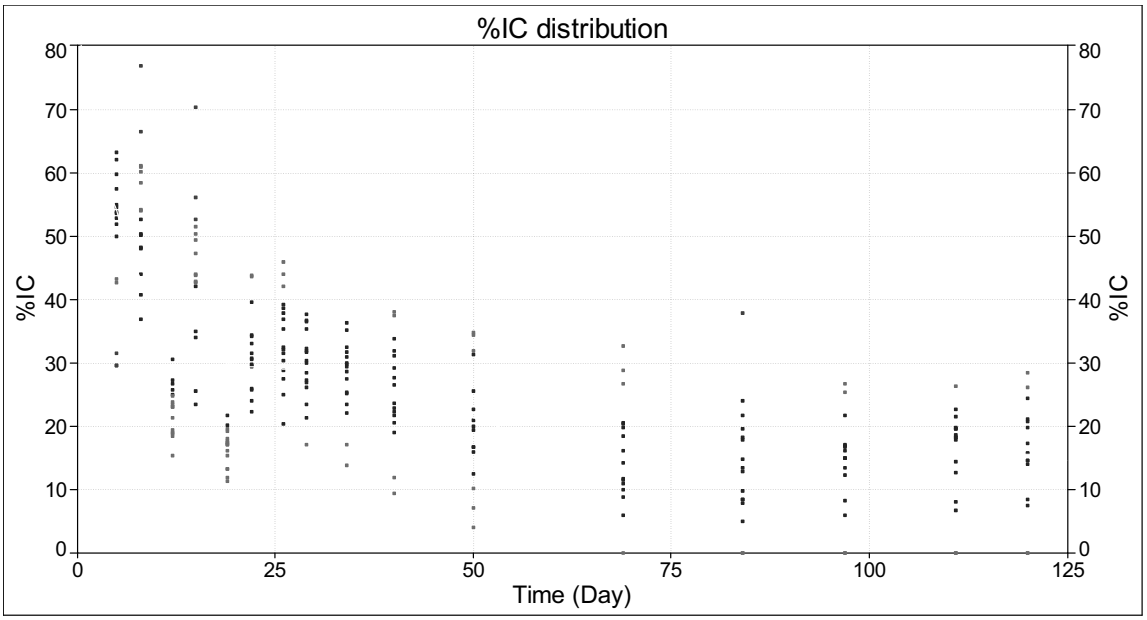

Fig. 23. Behavior of IC (percentage) during the decomposition process.

3.1.2.8. NO_x results

Nitrogen is an essential element in any organism and it is a major compound in cell wall components, nucleic acids and a key building block of protein molecule. Nitrogen is often the most limiting nutrient in soil and water and is vital for organism growth. The measurement of soluble nitrogen compounds in the leached solution indicate the release of this compounds form the decomposing plant and its consumption by microorganisms.

Nitrate concentration distribution in the leached solution of all the samples is plotted in Fig. 24 and it indicates that the maximum release of NO_3^- occurs after 15 days at least. The decline of the NO_3^- concentration does not necessarily mean that less NO_3^- is released from the decomposed plant to the soluble fraction but it is related to the consumption of this compound by microorganisms that grow in the leached solution. Therefore, measuring nitrogen compounds in decomposition experiments is related to microorganism growth. It is known that bacteria use nitrogen in the form of NH_4^+ or NO_3^-. Nitrate and nitrite, which are a simple nitrogen source, are charged molecules, which should not be able to cross biological membranes at fast rates. Nitrite may be able to cross biological membranes at significant rates in its protonated form even at neutral pH by passive diffusion. However, early evidence indicates that nitrate transport does require a specific transporter. Assimilation of nitrate (and nitrite) can be done via two types of uptake systems: ABC transporters that are driven by ATP hydrolysis, and secondary transporters reliant on a proton motive force (Moir and Wood, 2001).

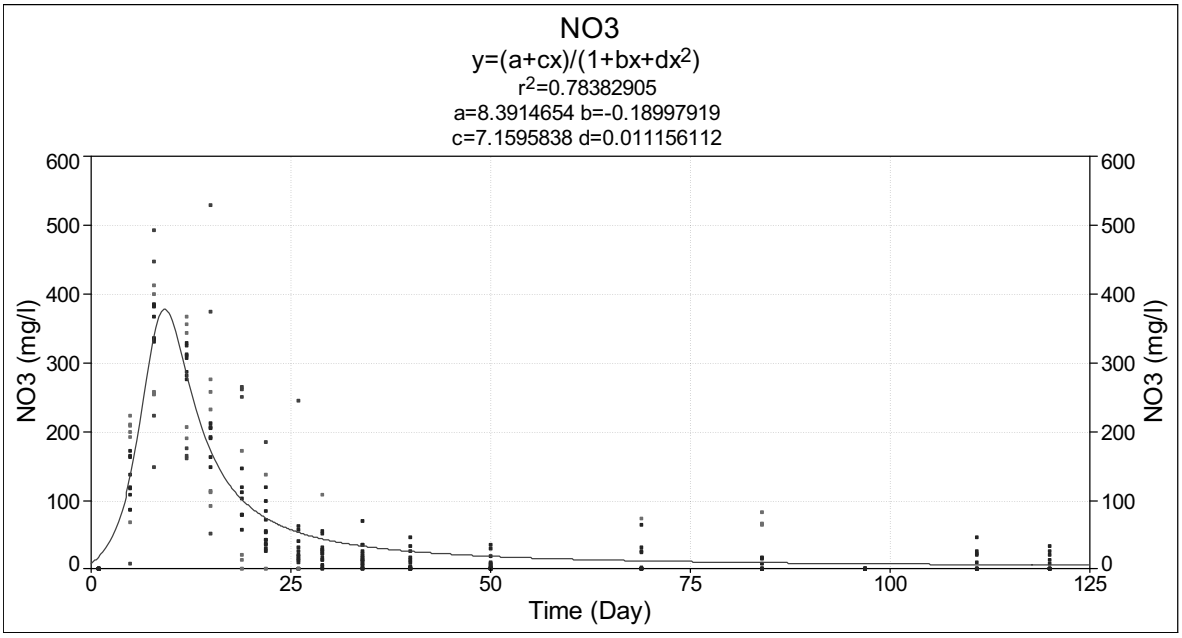

Fig. 24. NO_3 release during decomposition process.

Nitrite concentrations in the soluble fraction are shown in Fig. 25. No high correlation coefficient (R^2) was found. The lack of correlation indicates that transformations of nitrite occur. As a result measuring nitrite does not give viable data regarding decomposition in the examined decomposition apparatus.

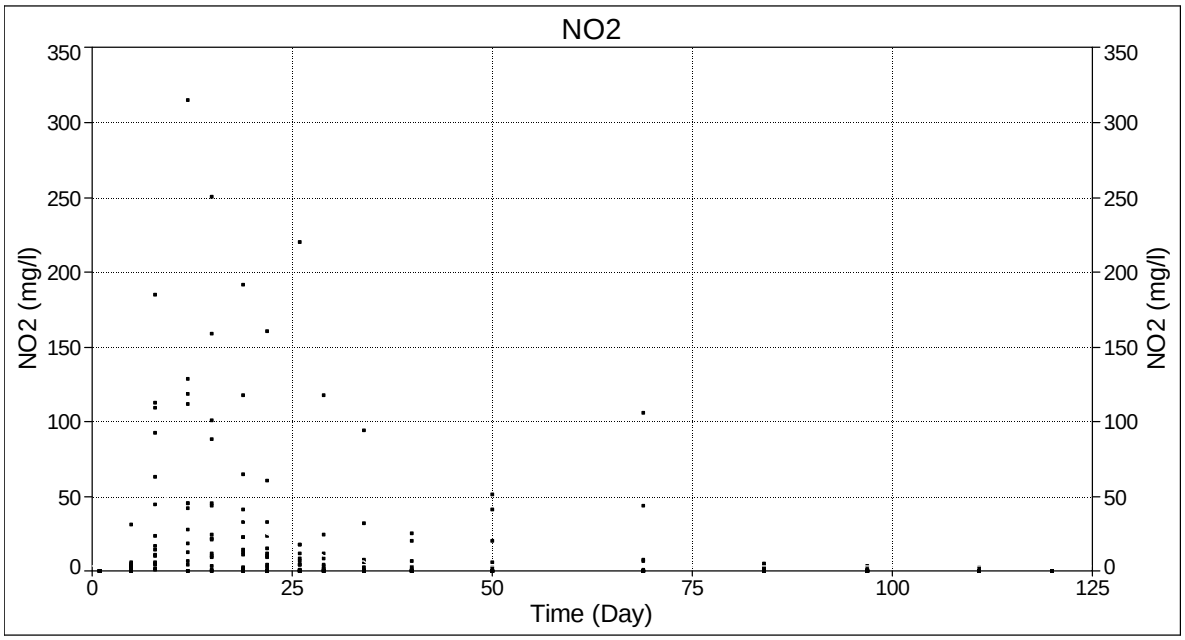

Fig. 25. NO_2 release during decomposition process.

3.1.2.9. SO_4 results

Sulfur is an important element in biogeochemical cycles. Sulfur exists in a variety of inorganic forms and the transformation between them is due to microorganism activity, which not all of them are decomposers (Swift et al., 1979). It is required for some amino acids in plants, animals, and microbes and is used for energy gain by microorganisms. Cysteine and methionine are essential building blocks of protein biosynthesis in all living organisms. These amino acids and the sulfur-containing cofactors (e.g. glutathione) must either be synthesized by the cell, or recruited by bacteria from the environment. The necessary sulfur for the biosynthetic process may be obtained also from inorganic form (e.g. as sulfate). Most of the sulfate and organosulfur transport systems that have been identified in bacteria are members of the ATP binding cassette (ABC) superfamily, which requires energy (Kertesz, 2001).

Sulfate is supplied to the microorganisms via the leached fraction. All the data were within the same internal span regardless to the gradient amount of bromine supplemented in the plant growth solution. Therefore, all the data was plotted as shown in Fig. 26. The leached sulfate from all the plants and groups indicate that the maximum release occurs within the first two weeks. Minor discrepancies occur due to the fragmentation procedure as already noticed in the

leached bromine. After two weeks the amount of sulfate in the leached fraction declines. The sulfate pattern is similar to nitrate and indicates that the microorganisms in the fraction are using the sulfate as a sulfur source. The result does not imply that there is no sulfate flow form the plant debris but rapid consumption by microorganisms is more likely.

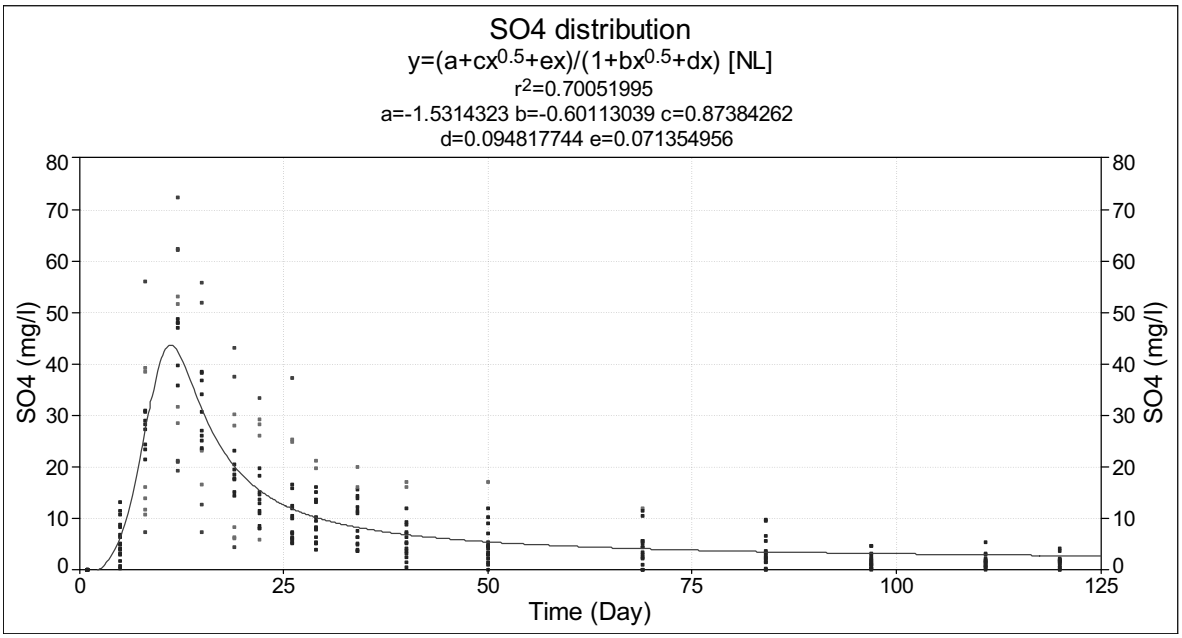

Fig. 26. SO_4 release during decomposition process.

3.2. Iodine experiment

3.2.1. Growth analysis

3.2.1.1. Physical dimension parameters

Physical dimension data (total length [cm], root length [cm], leaf length [cm] and root/leaf ratio) were analyzed for each plant and are presented in Table 13. One Way Analysis of Variance (ANOVA) of all the parameters indicate that the differences in the mean values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability. Hence there is no statistically significant difference in the examined parameters. Iodine in the examined concentration did not influence growth.

Table 13. Plant physical dimensions after treatment with iodine.

I. conc. in nutrient solution (mg/l)	Plant code	Total length (cm)	Root length (cm)	Leaf length (cm)	Root/Leaf ratio
Control	Icon1A	79	25	54	0.46
	Icon2A	100	42	58	0.72
	Icon1B	100	44	56	0.79
	Icon2B	113	59	54	1.09
	Average	98 ± 14	42.5 ± 13.9	55.5 ± 1.9	0.77 ± 0.26
0.05 mg/l	I11A	113	49	64	0.77
	I12A	111	62	49	1.27
	I11B	80	24	56	0.43
	I11B	87	35	52	0.67
	Average	97.8 ± 16.7	42.5 ± 16.5	55.3 ± 6.5	0.79 ± 0.35
0.5 mg/l	I21A	107	44	63	0.70
	I21B	104	45.5	58.5	0.78
	I22A	106	51	55	0.93
	I22B	109	45	64	0.70
	Average	106 ± 2.1	46.4 ± 3.2	60.1 ± 4.2	0.78 ± 0.11
5 mg/l	I31A	111	50	61	0.82
	I31B	111	44	67	0.66
	I32A	85	34	51	0.67
	I32B	94	50	44	1.14
	Average	100 ± 13	44.5 ± 7.5	55.8 ± 10.2	0.82 ± 0.22

3.2.1.2. Iodine uptake by *Lolium multiflorum*

The plants were exposed to different iodine concentrations in the growth solution (control, 0.05 mg/l and 0.5 mg/l). The uptake results are shown in Table 14. The control plants contained 1.13 ± 0.2 mg/kg which originates from the low amount found in the growth solution (2.6 ± 1 µg/l, n=5). The iodine source in the nutrient solution is the chemicals which comprise it.

The uptake of iodine was lower compared to the same bromine concentration used in the previous experiment, the control plants and the plants grown with 0.05 µg/l and 0.5 µg/l bromine were lower by 60%, 48% and 72% respectively. It is known that plants accumulate less iodine and fluorine, then chlorine and bromine uptake (Mackowiak and Grossl, 1999). A possible explanation may be related to the different uptake mechanisms used by the plants to take up

(actively/passively) various halides. Chlorine is essential for photosynthesis, bromine can be taken up passively due to its size while iodine is a rather big ion which has no known biological activity in terrestrial plants. Unfortunately, the available knowledge falls short to explain this difference.

Grasses are known to contain iodine in the range of 0.03-7.1 mg/kg (Fuge and Johnson, 1986; Kabata-Pendias and Pendias, 2000). The plants that were treated with 0.05, 0.5 mg/l iodine contain a relative high amount of iodine compared to nature. Consequently, the plants that were cultivated without iodine resemble natural plants. This results emphasis that in nature the iodine uptake is dependent on the iodine distribution and availability in soil, Mackowiak and Grossl (1999) cited that as the valency and molecular weight of the iodine species increase the overall iodine uptake decreases.

Table 14. Iodine uptake by *Lolium multiflorum*.

Iodine conc. in nutrient solution (mg/l)	Plant code	I conc. in plant (mg/kg)
Control	Icon1A	1.3
	Icon2A	0.9
	Icon1B	1.2
	Average	1.13 ± 0.21
0.05 mg/l	I11A	33.3
	I12A	40.2
	I11B	20.9
	Average	31.5 ± 9.78
0.5 mg/l	I21A	116
	I21B	181
	I22A	135
	Average	144 ± 33.4

3.2.1.3. Water content in plants

As described in the materials and methods section (2.2.1) the plants were cut according to their Y-axis, one part of the each plant was weighed before and after freeze drying in order to determine the amount of water. The water percentage results that are shown in Table 15 indicate a total average of 94.3, which is higher compared to the bromine water percentage (73%). The difference might indicate that toxicity of bromine is higher then toxicity of iodine which has an

effect on the plants' water content (the plants were harvested at the same age). Another reason might be the freeze dryer efficiency.

Table 15. Average plant water percentage.

Plant code	Total sample weight (g)		%Water
	Before freeze dryer	After freeze dryer	
IconXY	33.2 ± 26	2.1 ± 1.77	93.9 ± 0.4
I1XY	28.6 ± 6.73	1.61 ± 0.37	94.4 ± 0.06
I2XY	38.8 ± 21	2.19 ± 1.38	94.7 ± 0.9
All samples average	38 ± 12	9.8 ± 2.7	94.3 ± 0.61

3.2.1.4. Overall iodine concentration in the plants

In order to calculate the amount of iodine in the entire plant the same calculation as in section 3.1.1.5 was applied. The results for each plant are shown in Table 16. From the results it can be noticed that the standard deviation of plant iodine concentration in a group treatment can be up to 69%. The dissimilarity can be the result of a different uptake rate. It is known that the uptake rate via the root zone is influenced by various factors such as rhizosphere processes and influence of microorganisms on bioavailability, ions concentration in the root system, etc (Ehlken and Kirchner, 2002). In the case of iodine, its uptake can be passive which will result in lower uptake rates which will increase as the iodine concentration outside the plant will rise.

Table 16. Calculated iodine content in iodine enriched plants.

Plant code	%Water	TW-Total weight (g)	I conc. (µg/g)	CDW- Calculated dry weight (g)	CIC - Calculated I content (µg)*
Icon1A	93.8	36.3	1.3	2.40	3.12
Icon2A	94.3	38.6	0.9	2.20	1.98
Icon1B	93.5	91.7	1.2	6.05	7.26
Average	93.9 ± 0.4	55.5 ± 31.3	1.13 ± 0.21	3.55 ± 2.17	4.12 ± 2.78
I11A	94.3	39.3	33.3	2.24	74.6
I12A	94.4	48.9	40.2	2.74	110
I11B	94.4	34.8	20.9	1.95	40.7
Average	94.4 ± 0.06	41 ± 7	31.5 ± 9.78	2.31 ± 0.4	75.1 ± 34.7
I21A	94.1	86.3	116	5.09	591
I21B	95.7	27.2	181	1.17	211
I22A	94.2	61.4	135	3.56	480
Average	94.7 ± 0.9	58.3 ± 29.7	144 ± 33.4	3.27 ± 1.98	428 ± 195

* Iodine amount calculation for the entire plant and based on dry weight

3.2.1.5. Iodine concentration in decomposed plant parts

The same calculation and assumption as in section 3.2.1.4 were applied. Though, the calculation is based on the wet weight of the decomposed part. The calculation is shown in Table 17.
Iodine concentration differences are lower in the decomposed part of the plant compared to the concentration in the entire plant. The results emphasize the lower plant uptake rate but the effects are lower due to smaller biomass examined.

Table 17. Iodine concentration in the decomposed plant parts.

Plant code	%Water	DW-Decompose weight (g)	I conc. (µg/g)	CDW-Cal. dry weight (g)	DCIC-Decomp. Cal. I content (µg)
Icon1A	93.8	19.2	1.3	1.19	1.55
Icon2A	94.3	19.3	0.9	1.10	0.99
Icon1B	93.5	28.5	1.2	1.87	2.24
Average	93.9 ± 0.4	22.3 ± 5.3	1.13 ± 0.21	1.38 ± 0.42	1.59 ± 0.63
I11A	94.3	10.7	33.3	0.61	20.2
I12A	94.4	13.5	40.2	0.75	30.3
I11B	94.4	12.9	20.9	0.73	15.2
Average	94.4 ± 0.06	12.4 ± 1.5	31.5 ± 9.78	0.7 ± 0.08	21.9 ± 7.73
I21A	94.1	28.2	116	1.67	194
I21B	95.7	10.6	181	0.46	82.6
I22A	94.2	19.8	135	1.15	155
Average	94.7 ± 0.9	19.5 ± 8.8	144.0 ± 33.4	1.09 ± 0.61	143.6 ± 56.3

3.2.2. Decomposition of iodine enriched plants

3.2.2.1. Decomposition of control plants

The iodine concentration and species during the 75 days of decomposition are shown in Fig. 27. The graphs are presented in the following order: graph 27A shows the concentration of iodine in the leached fraction, graph 27B shows the organoiodine concentration versus the total iodine concentration in the leached fraction and graph 27C shows the percentage of organoiodine and inorganic iodine from the total iodine in the leached fraction. The figure structure will be repetitive during the whole section.

From the results of the first control plant shown in Fig 27A it can be noticed that the release of iodine occurred throughout all the examined period and without an apparent release pattern. Compared to the decomposition of the bromine control plant the lack of a pattern is noticeable and the release is lower by two factors. Most of the leached solutions contain ~10% and less inorganic iodine, only in days 9, 19, 23 the inorganic fraction was 44% (average of these days). The rise in the iodine inorganic fraction at specific days can be related to release of inorganic iodine stored in the plant or from transformation of iodine in the leached solution (Amachi et al., 2001; Muramatsu and Yoshida, 1999). Unlike bromine, where the initial release from the decayed material was always as inorganic species and by that indicting their species in the plant, the iodine control plant results indicate the presence of inorganic and organic iodine species in the plant. Unfortunately, no iodine speciation in terrestrial plants is available. Iodine speciation in brown algae (*Laminaria* spp.) indicates that it can be present as an anion and incorporated in aromatic compounds (when *Laminaria* spp. freeze dried cells are rehydrated in diluted hydrogen peroxide). Furthermore, subtle changes in the Extended X-ray Absorption Fine Structure (EXAFS) spectra are observed when intact cells are exposed to oxidative stress, which can be caused by elicitors (Feiters et al., 2002).

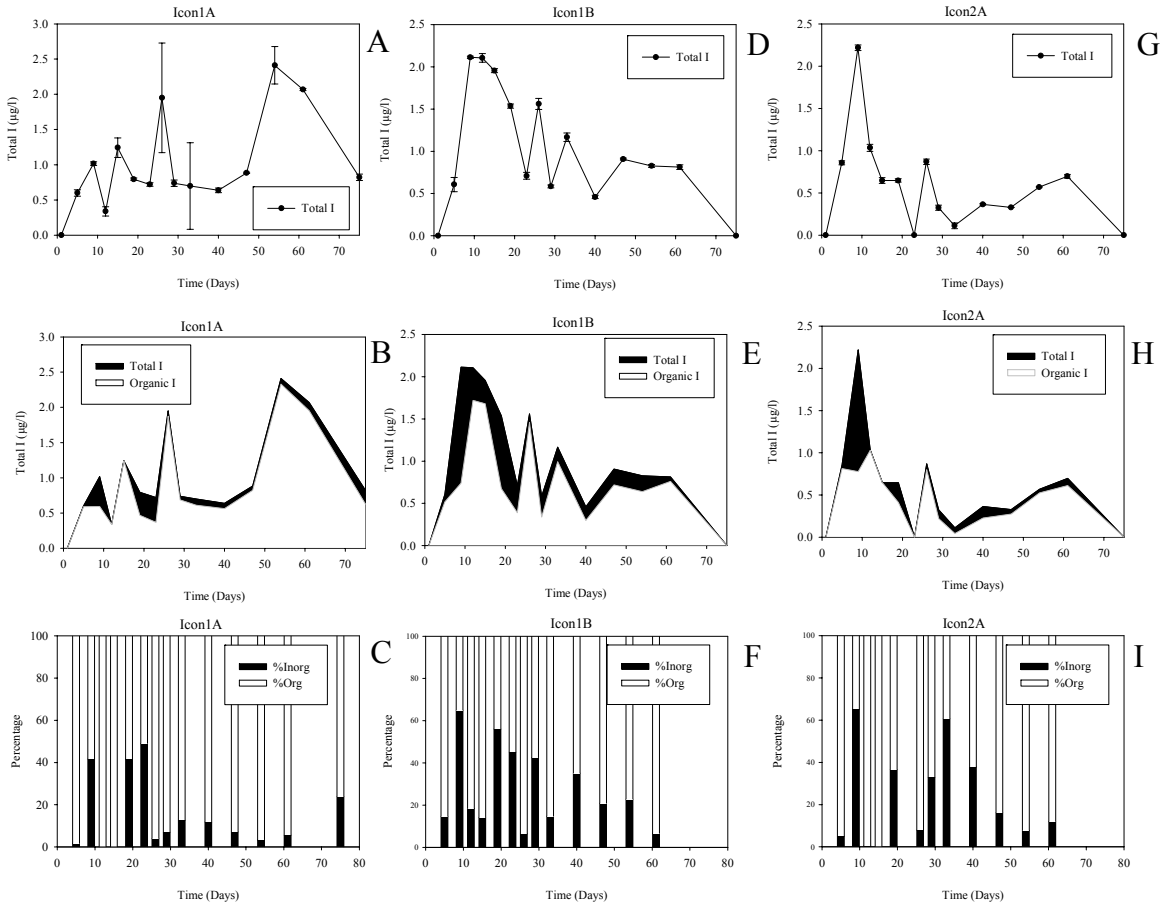

Fig. 27. Iodine concentration and speciation of control plants leached fraction during 75 days of decomposition.

The second control plant (Icon1B, graph 27D, E, F) displays a different release pattern form the previously examined control plant. The iodine release in this control plant displays multiple peak events that occur in several days (9, 26, 33, and 47), the peaks are related to the iodine low concentration release from the decay plant. Again, shifting in inorganic-organic species occurs during the decomposition period. The third control plant (Icon2A, graph 27G, H, I) shows a similar release pattern as the second plant.

The low concentration of the iodine release during the control plants decay does not provide enough data to explain the behavior and pattern of the leached iodine.

3.2.2.2. Decomposition of plants grown with 0.05 mg/l iodine

Decomposition results of the plants grown with 0.05 mg/l supplemented iodine are shown in Fig. 28. The leaching processes patterns are clearer and repetitive unlike the control plants, emphasizing the importance of plant iodine concentration. In the first plant examined, maximum release occurred at day 9 of the experiments (graph 28A, B, C), and declines as the

decomposition time proceeds (75 days). The inorganic-organic ratio speciation reveals that like from the control plants, iodine is released as organic fraction with some increases in the inorganic iodine content (day 9, 19). The second plant (I11B) (graph 28D, E, F) and the third plant (graph 28G, H, I) (I12A) show similar behavior in all the parameters examined, with maximum release within two weeks, although plant three had lower concentrations reflecting the lower iodine amount in the plant (40.2 mg/kg vs. 20.9 mg/kg).

In all the leached solutions a dynamics in the inorganic-organic speciation occurs, which is represented by an increase, decrease, increase and again decrease of organoiodine during the first three week (in plant I12A it occurred 3 times). The reason for this dynamic can be related to the iodine amount and species released from the plant, microbial transformation and fragmentation effects. The breaching events of the decay plant cell walls cause a discharge of the cell content versatile compounds during decomposition, these compounds may be organoiodine, inorganic iodine but in addition a reaction between organic compounds and inorganic iodine species can occur. The presence of microorganisms in the leached fraction is certain, the microorganism can synthesize or degraded organoiodine compounds.

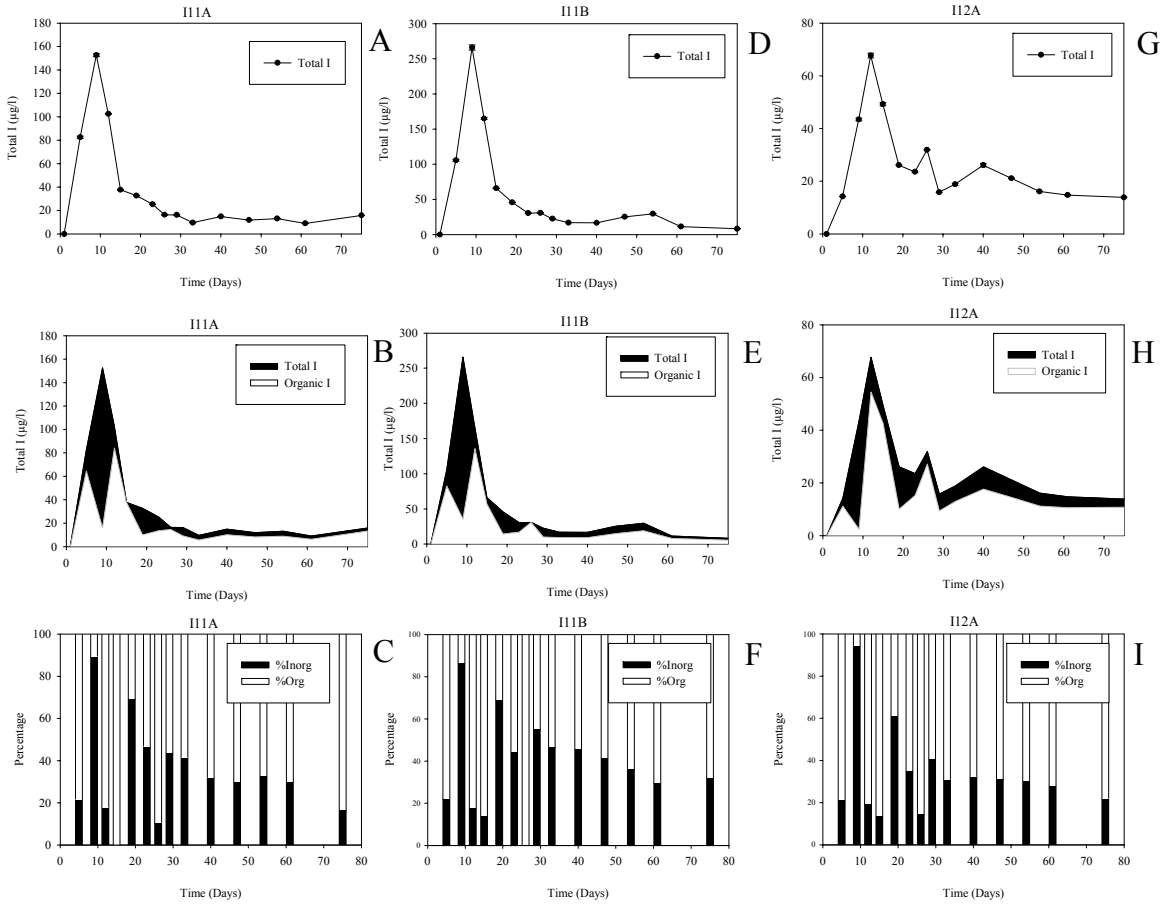

Fig. 28. Iodine concentration and speciation of 0.05 mg/l plants during 75 days of decomposition.

3.2.2.3. Decomposition of plants grown with 0.5 mg/l iodine

The leaching results are shown in Fig. 29, the release pattern is similar to the decomposition of plants grown with 0.05 mg/l iodine. Maximum iodine release occurred at day 9 of the experiment and was followed by a decline until the experiment ended. The speciation results reveal the same peak phenomena and a decrease in the inorganic fraction as a function of time which occur in all the three examined plants although in different concentrations. Again, compared to the decay of plants grown with the same concentration of bromide, the released of iodine is in both organic and inorganic species (bromine release only inorganic species).

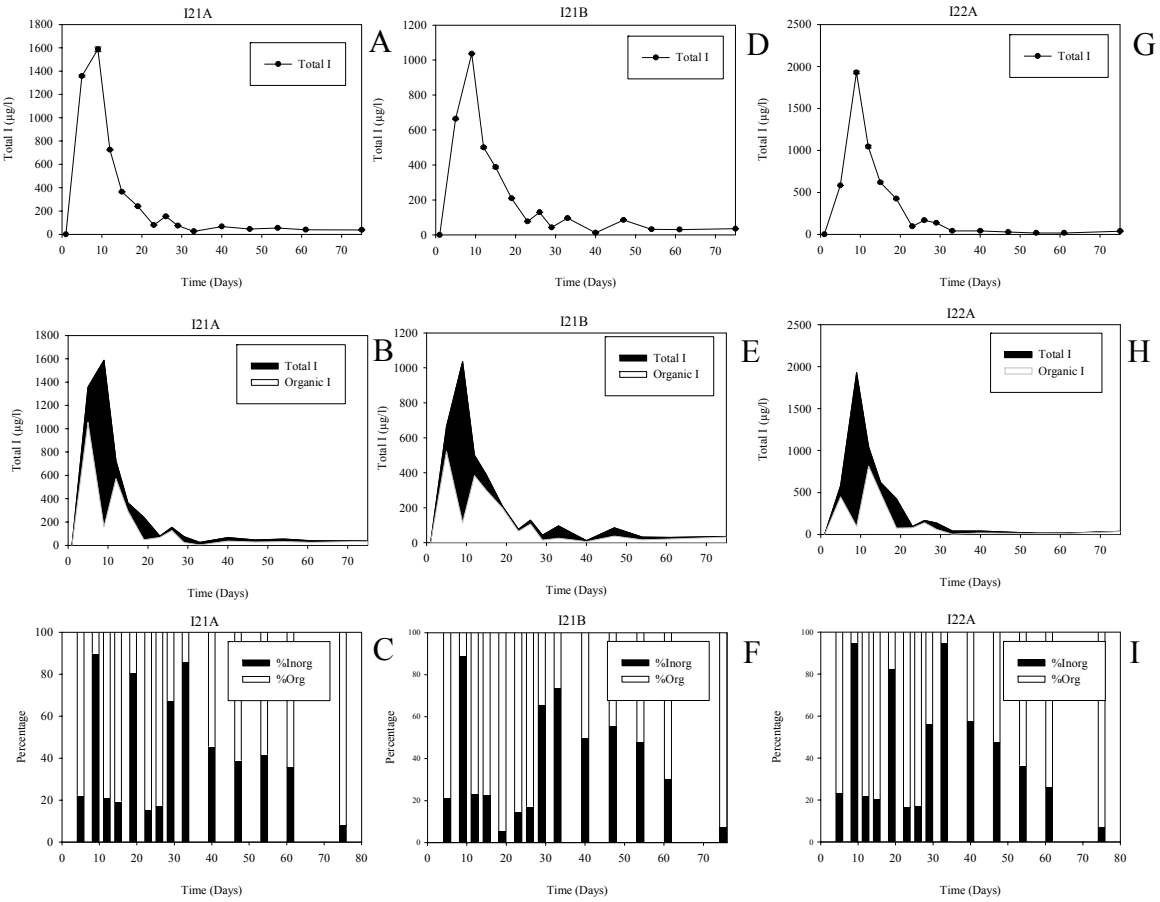

Fig. 29. Iodine concentration and speciation 0.5 mg/l plants during 75 days of decomposition.

3.2.2.4. Iodine decomposition summary

The measurements show that the average iodine release from the plants is a function of the initial iodine concentration. The release pattern was identical in the plants that were grown with 0.05µg/l and 0.5 µg/l iodine, while the iodine release pattern form the control plants were similar to “noise” due to the very low concentrations. The presence of inorganic and organic iodine in

the beginning of the decomposition is related to the species storage form in the plant (both species).

3.2.2.5. Iodine mass balance

Similar to the bromine mass balance calculation (section 3.1.2.6) the mass balance was calculated for iodine and is shown in Table 18. Examination of the data reveals that the iodine amount leached (%) from the control plants to the solution varies between each plant (28.3% ± 17.3). The differences in the iodine leached percentages are a result of different iodine amounts in every individual control plant. The iodine uptake by plants in low concentrations is not efficient. The iodine percentage leached data shows that the plant with the minimum initial iodine amount (µg) leached more iodine (%) (Icon1B (0.99µg, 45.5%) < Icon1A (1.55 µg, 28.1%) < (Icon2A (2.24 µg, 11.1%)). The relative iodine amount which remains in the plant is low. Once again, the lower the initial amount of iodine in the plant the higher the amount of iodine which will remain in the decomposed plant (Icon1B<Icon1A<Icon2A). The volatile fraction shows an opposite pattern and the plant with the highest initial iodine amount (Icon2A (2.24 µg)) released the most iodine volatile species. The results show that iodine can be in all the three fractions: volatile, in solution (leached) and bound to organic matter (remain in the plant). The decomposition vessels were exposed to the same environmental conditions and the decomposition process was similar emphasising that the initial amount is a crucial factor to the fate of iodine during this process.

Decomposition of plants that were grown with 0.05 mg/l iodine shows less distinct in the value of all the three fractions (leached, remained, volatilized) in between the plant treatment, a result of the higher iodine amount in these plant group. The remaining percentage of iodine in the plant after the decomposition resembles the control treatment plants. The leached percentage is higher by a maximum of 6 times compared to the control plant. The plant in this group that had the highest iodine amount (I11B, 30.3µg) also released the highest amount to the leached fraction (73.9%). The iodine volatilization in this plant group is low, the difference can be up to ~21% compared to the control group. It seems that when the plants have a pronounced amount of iodine most of the iodine is not volatile and is released to the leaching solution. This is a contradiction to bromine experiments where most of the bromine was volatilized.

Decomposition of plants that were grown with 0.5 mg/l iodine shows an interesting phenomenon, no performable mass balance is possible for two (out of the three) decomposed plants (I21A, I22A). The plant with the maximum initial iodine amount (I21A, 194 µg) releases 8% as volatile and ~78% were leached out. Similar to the results of the plants that were grown

with lower iodine concentration (0.0.5 µg/l). In plants I21A and I22B the iodine amount released from the plants adds up to more then 100% although the amounts remaining in the plants are comparable to the other experiments (decomposition of other iodine enriched plants). The reason for this unbalance is related to a dilution factor issue and to the experiment running time. In order to measure iodine in these high concentrations a dilution was performed in order to measure the concentration with ICP-MS, the dilution caused the inaccuracy. The running time of the experiment (75 days) was shorter than the one for bromine (125 days), possibly indicating that the decomposition system did not achieve steady state and the complex processes occurring during decomposition were still in progress (e.g. release of cell content, microbial attack on the plant debris). The lack of a steady state affects the on-going iodine release and transformations in the decomposing apparatus, this indicates that some species might require more time to be released/volatilized during plant decomposition. Like for bromine, the iodine volatile fraction was not specified. Methyl Iodide (CH_3I) is a gas that can be formed by decomposition processes and is produced by biomethylation processes (Thayer, 2002) in organisms such as bacteria (Muramatsu et al., 2004). Lower amounts of volatile iodine were produced compared to volatile bromine indicating that the present microorganisms were not efficient in creating methyl iodide or other volatile iodine compounds. In addition, methyl bromide boiling point is lower compared to methyl iodide (3.6°C and 40°C, respectively) which affect its volatilization.

Table 18. Iodine mass balance.

Fraction	Contorl				0.05 mg/l				0.5 mg/l			
	Icon1A	Icon1B	Icon2A	Average	I11A	I11B	I12A	Average	I21A	I21B	I22A	Average
% Leached	28.1	45.5	11.1	28.3 ± 17.2	69.4	73.9	65.3	69.5 ± 4.3	78.2	120	107	101 ± 21
%Remain in plant	21.8	24.6	12.3	19.6 ± 6.45	18.2	22.5	26.2	22.3 ± 4.06	13.8	28.5	16.5	19.6 ± 7.81
% Volatile	50.1	29.9	76.6	52.2 ± 23.4	12.4	3.6	8.5	8.2 ± 4.4	8	n.a.	n.a.	n.a.
Initial iodine amount in plant (µg)	1.55	0.99	2.24	1.59 ± 0.63	20.2	30.3	15.2	21.9 ± 7.73	194	82.6	155	143 ± 56

* n.a. – not available.

3.3. Atlantic beech (*Fagus Sylvatica*) experiment

3.3.1. Bromine concentration and water content in *Fagus Sylvatica* leaves

Atlantic beech (*Fagus Sylvatica*) leaves were weighed before and after freeze drying in order to determine the bromine concentration and the amount of water. The amount of bromine in leaves

was 3.4 mg/kg (dry weight). The water percentage was 84 percent while for *Lolium multiflorum* grown under bromine or iodine regime, the water percentage was 73%, 94% respectively. The difference shows that different species under different environmental conditions contain a different amount of water.

3.3.2. Total bromine concentration in *Fagus Sylvatica* leaves

In order to calculate the bromine amount in the *Fagus Sylvatica* leaves the same calculation applied in section 3.1.1.6 was carried out. The results for leaf sets are shown in Table 19.

Table 19. Calculated bromine content in *Fagus Sylvatica* leaves.

Set code	%Water	TW-Total weight (g)	Br conc. (µg/g)	CDW- Calculated dry weight (g)	CBC - Calculated Br content (µg)
RW1	84	5.8	3.4	0.9	3.2
RW2	84	5.4	3.4	0.9	2.9
RW3	84	7.3	3.4	1.2	4.0
RW4	84	4.4	3.4	0.7	2.4
Average	84	5.7 ± 1.2	3.4	0.9 ± 0.2	3.1 ± 0.6

3.3.3. Decomposition of *Fagus Sylvatica* leaves

The leaf set decomposition conditions were similar to the previous decomposition experiments. The total bromine release pattern of all the leaf sets is shown in Fig. 30.

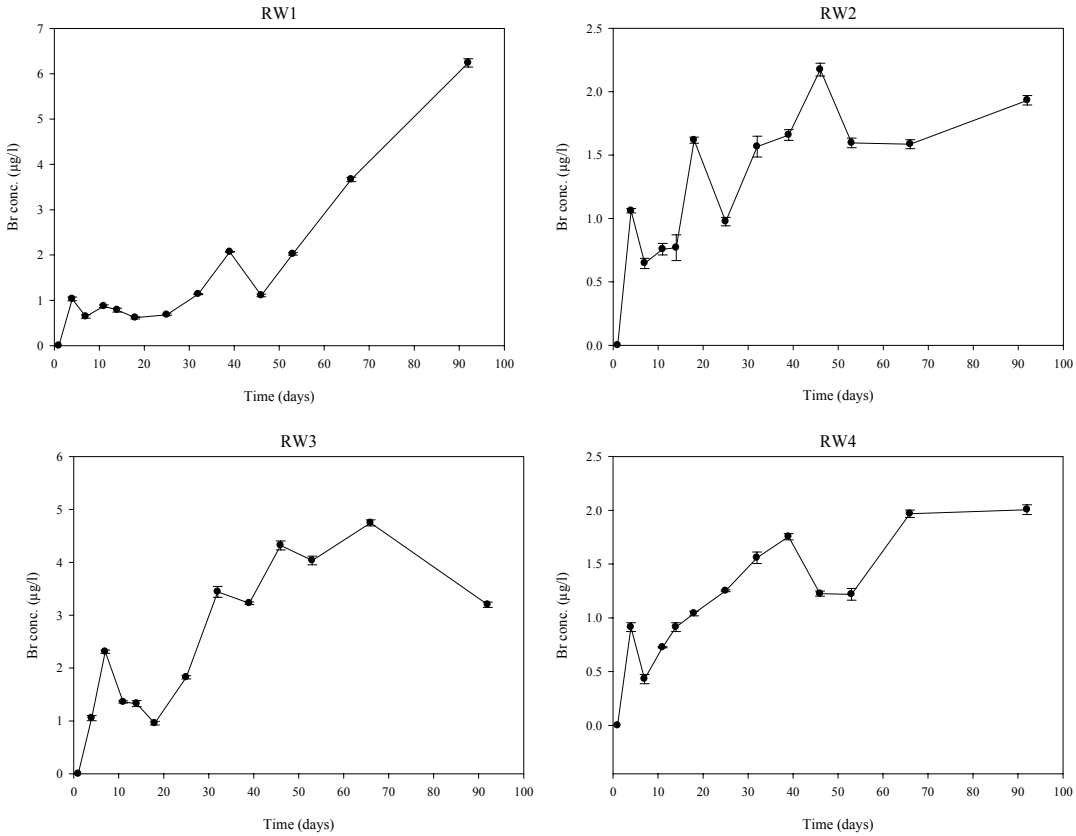

Fig. 30. Bromine concentration in the leached fraction of *Fagus Sylvatica* leaves during 92 days of decomposition.

In the first leaf set (RW1) it seems that the bromine amount releases is low until day 39. The release is low since the leaves were not cut and decomposing microorganisms require more time to breach the cell wall of the leaves. The increase that occurs after day 39 is the result of the cell content which is released.

The second leaf set (RW2) shows the same pattern but the concentrations are lower compared to the first set. The bromine concentration increase in the leached solution is due to the release of cell content due to the degradation abilities of the microorganisms. The other sets (RW3, RW4) show a similar pattern of bromine release.

Compared to the *Lolium multiflorum* release pattern were a release in the first two weeks from the beginning of the decomposition was noticed, the *Fagus Sylvatica* leaves bromine release patterns in all the sets does not show a decline. This pattern indicates that the process is still underway. The dissimilarity in the decomposition rates are due to the different leaf properties (structure, chemical content), preparation of the plant prior to decomposition (no preliminary cutting), different secondary metabolites that influence the microorganisms growth and diversity, and lower bromine concentration, which linger the release of bromine for the leaves. If the decomposition would have been performed for a longer time period a peak shape pattern could

be noticed but decomposition is a process that can take long time. Leaf litter of *Fagus Sylvatica* showed a in previous study a low loss rate during decay processes (Swift et al, 1973).
Iodine decomposition were also examined and the release concentrations from the leaf sets were very low (0.26 ± 0.17 µg/l).

3.3.4. Bromine mass balance

Bromine mass balance for other species (*Lolium multiflorum*) grown under lab conditions was shown in section 3.1.2.6. The same concept and calculation was applied on *Fagus Sylvatica* leaves collected from a sampling site (a detailed examination of the halogens in the study sites is given in section 3.4). The results of the *Fagus Sylvatica* leaves bromine decomposition mass balance are shown in Table 20.
The bromine mass balance reveals that due to the low decomposition rate most of the bromine is still stored in the plant (68.1% ± 6.5). In the decomposition period the microorganisms did not penetrate most of the plant cells. As a result the bromine concentration in the leached fraction is relatively low (18.9% ± 3.3) and the amount of bromine volatile percentage is also low (12.9% ± 6.1). In a previous section (3.1.2.6), a possible volatile species has been discussed (CH_3Br).

Table 20. *Fagus Sylvatica* leaves decomposition - bromine mass balance.

Fraction	RW1	RW2	RW3	Average
% Leached	18.4	15.9	22.5	18.9 ± 3.3
% Remain in plant	75.5	66.1	62.9	68.1 ± 6.5
% Volatile	6.1	18	14.6	12.9 ± 6.1
Initial iodine amount in plant (µg)	3.2	2.9	4.0	3.4 ± 0.5

The implementation of the *Fagus Sylvatica* leaves decomposition on the bromine cycle in soil are of great interest since the amount of bromine which is not volatilized during the natural decomposition period is entering the soil.

3.4. Halogens in forest ecosystems

Iodine and bromine in soil are known to be originated from atmospheric deposition and from weathering of parent material. Prior results indicated that iodine and bromine can return to soil via litter decomposition (following a halogen accumulation in leaves during the growth period), although in lower amount due to loss by volatilization. Iodine and bromine concentrations were measured at two forest sites. The measurements covered vegetation, rocks, soil and atmospheric deposition in order to understand the behavior of iodine and bromine in a forest ecosystem.

3.4.1. Halogens concentration in rain, snow and atmospheric flux

The annual precipitation in the vicinity of Heidelberg is 761mm (Raum Mannheim/Heidelberg 2001/2002). Bromine concentrations in rain were 2.5 ± 0.4 µg/l and in snow 3.3 ± 0.9 µg/l (n=3) while iodine concentrations in rain were 0.38 ± 0.01 µg/l and in snow 1.18 ± 0.5 µg/l (n=3). Noticeably, bromine concentrations in rain are up to 6.6 times higher than those of iodine. The annual amount of bromine entering the soil via precipitation is 1.9 mg/m^2·year and for iodine the amount is 0.3 mg/m^2·year.

The known I/Br ratio in sea water is 0.00117 (Duce et al., 1965) while in aerosol and rain the ratio is 0.14 and 0.20 respectively (Duce et al., 1963). The I/Br ratio in sea water is lower compared to aerosol reflecting the enrichment of iodine. Iodine is enriched in aerosols due to two possible mechanisms, Iodine bound to organics in a surface active film on the ocean or a photochemical source in the gas phase followed by condensation on aerosols (Murphy et al., 1997).

The I/Br ratio at the Heidelberg site in rain is 0.15, it is higher than the seawater ratio and lies between the known ratio of aerosols and rain water. Although the number of samples examined is three, the examined ratio implies that the halogens in deposition at this site originate from marine source.

3.4.2. Halogens concentration in bedrock

In order to inspect if both halogens are originating from bedrock, an analysis of their content in rocks was performed. The bromine concentration in Carbonate site rocks (limestones, 5.8 mg/kg) is more than five times higher then in the Sandstone site rocks (sandstone, 1.1 mg/kg), the data is shown in table 21. The content in the rocks indicate that limestone weathering can increase soil bromine content. Unfortunately, the amount of iodine in both rock types is below INAA

detection limit (<1 mg/kg) but data from Muramatsu and Wedepohl (1998) showed that the iodine concentration in limestones (1793 µg/kg, mean of average, n=7) is higher than in sandstones (116 µg/kg, mean of average, n=3). As a result, during limestone weathering iodine is also released to the soil, but other analytical methods (e.g. RNAA) would be necessary to quantify the contribution.

3.4.3. Halogens concentration in tree leaves and leaf decomposition products

Halogen concentrations in Atlantic beech (*Fagus Sylvatica*) leaves, leaf litter as well as rocks and soil are shown Table 21. The Atlantic beech tree can uptake the halogens from deeper sections of the soil (mineral horizon) via the roots and transfer them to the canopy via the xylem. Bromine concentrations in the leaves were not constant during the period examined at both sites, the concentrations ranged from 0.4 to 1.7 mg/kg. The iodine concentration in the leaves during the growth period is also inconsistent and starts form <1 mg/kg to a max of 4.3 mg/kg.

Fluctuation in plant iodine and bromine concentrations in leaves during the season are reported in previous works (Kabata-Pendias and Pendias, 2001, Wilkins, 1978), and are related to deposition of sea-spray (unlikely, in this case) or to fluctuation in the bromine concentrations in precipitation, which affects the pattern of uptake by the plant from the soil. In addition, the uptake of the halogens by the plant is affected by their bioavailability in the soil. It is known that humic acids/organic matter reduce the iodine bioavailability (Mackowiak et al., 2004), a similar effect of organic matter is also possible with bromine.

Halogen concentrations in leaf litter layers are higher compared to tree leaves, bromine concentration in the litter can reach up to 6.8 mg/kg while iodine maximum concentration is 10.7 mg/kg.

The enrichment of halogens occurs probably because of the ability of microorganisms and fungi to synthesize, degrade and transform halogen compounds using enzymes such as haloperoxidases and perhydrolases (Verhagen et al., 1996; van Pée and Unversucht, 2003; Murphy, 2003). Furthermore, microorganisms in the leaf litter attack the leaf carbon structure, thus creating various by-products (organic matter) that are involved in the iodine and bromine sorbing processes. In addition, It is known that evaporation, plant uptake, and degassing may cause accumulation near the surface of the soil (Sheppard et al., 1994) but sorption processes of iodine in soil are dependent on iodine speciation, relative mineral and organic content, redox potential, pH and microbiological activity as well as interaction amongst them (Bostock et al., 2003).

Table 21. Bromine and Iodine content in tree leaves, leaf litter and rocks.

Sample name	Br (mg/kg) XRF	I (mg/kg) INAA
Sandstone site		
Rocks	1.1	<1
Tree leaves 5/04	0.4	1.0
Tree leaves 6/04	0.7	1.0
Tree leaves 7/04	0.9	4.3
Tree leaves 8/04	1.3	<1
Tree leaves 9/04	1.7	<1
Leaf litter upper layer	2.5	8.4
Leaf litter mid-layer	3.3	3.5
Leaf litter lower layer	6.8	10.7
Soil	5.3 ± 1.7	8.5 ± 3.5
Carbonate site		
Rocks	5.8	<1
Tree leaves 9/04	1.0	1.0
Leaf litter upper layer	2.8	4.5
Leaf litter mid-layer	5.9	7.8
Leaf litter lower layer	5.8	6.3
Soil	6.4 ± 1.4	7 ± 3

Abbreviations: X/04 means Month/2004.

3.4.4. Bromine and iodine in the examined soils

Bromine and iodine distribution in soil at the Sandstone site are shown in Fig. 31A, B. The bromine and iodine average concentrations in the Sandstone soil profiles are 5.3 ± 1.7 mg/kg and 8.5 ± 3.5 mg/kg, respectively.

At the top soil the halogens are originating from atmospheric deposition and litter decomposition. An increase in the soil halogen concentrations occurs until the end of the organic soil layer at section 15-20 cm, depth deeper to this layer the halogen concentrations deviate. The accumulation of the halogens in the top soil layers can be explained using the soil horizon classification and grain size analysis of the profiles (Table 22). Section 15-20 cm is the

beginning of the Bt horizon and has a lower percentage of sand and a high percentage of clay and silt compared to the upper layers. The high percentage of clay and silt fraction in section 15-20 cm hinders the movement of halogens below this section, causing them to accumulate in this section. An increase of halogens in the soil also occurs in section 30-35 cm, due to a change to Bv horizon. Another increase occurs at section 45-50 cm, the start of a Cv horizon.

Local podzolization processes were noticed in this site. The process encompasses the downward migration of organic matter, Al and Fe, from the surface areas and their accumulation in deeper areas of the profile. This process is characterized by an acidity that causes the slow development of organic matter and an alteration of the mineral phase, releasing abundant elements that are washed by the drainage waters, while the medium is enriched with insoluble elements (such as Fe and Al), which are migrated downward by the organic compounds towards deeper horizons. Quartz is fairly stable under acid conditions, it remains behind as a residue in the upper part of the mineral body (http://www.blm.gov).

Iodine and bromine distribution patterns in the cores are similar and no correlations have been found between the halogens and the total soil carbon which is show in Fig. 33 A, B.

Examined halogens distribution in the Carbonate site profiles are shown in Fig. 32A, B. The average bromine concentration is 6.3 ± 1.4 mg/kg while the average iodine concentration is 7 ± 3 mg/kg. Iodine and bromine distribution in a specific core are analogues but differ between the examined profiles, indicating that similar accumulation/mobility/formation processes are affecting them. In the upper soil horizons (Ao and Ah) a fluctuation in the halogen concentrations can be noticed. It is known that in A horizons the organic matter is well decomposed and is either distributed as fine particles or present in coating on mineral particles (FitzPatrick, 1980). The grain size analysis shows that until the section 8-10 cm (end of Ao horizon) the distribution between the fraction (sand and clay+silt) is equal. This might explain the accumulation of halogens in this section, since the followed section is the Ah horizon (section 10-15 cm) were the clay+silt fraction is increasing up to 80%. The clay+silt fraction remains in this percentage value until the end of the examined profile. At the end of the Ah horizon (section 25-30 cm) the halogens concentration decreases and the transition to the Bv horizon that follows shows an increase in the halogens concentration and is related to properties of the horizon which is formed from weathering processes. Pattern dissimilarity is observed between the two soil cores. No correlation can be found between the halogens and the total carbon (Fig. 33 C, D)

A summary of the results in this section indicates that the halogen distribution pattern merely follows the soil horizons and their respective clay and silt percentage. In addition, halogen concentrations in the mineral horizons are altered by weathering processes.

Table 22. Soil horizons and grain size distribution.

Site	Depth [cm]	Horizon	Sand fraction [%]	Clay and silt [%]	Site	Depth [cm]	Horizon	Sand fraction [%]	Clay and silt [%]
Sandstone	0-4	O	Leaf litter		**Carbonate**	0-5	O	Leaf litter	
	4-5	Ao	77	23		5-6	Ao	42	58
	5-7		72	28		6-8		45	56
	7-10		61	39		8-10		47	53
	10-15		58	42		10-15	Ah	18	82
	15-20	Bt	17	83		15-20		16	84
	20-25		62	38		20-25		12	88
	25-30		64	36		25-30	Bv	21	79
	30-35	Bv	68	32		30-35		13	87
	35-40		61	39		35-40		14	86
	40-45		55	45		40-45		13	87
	45-50	Cv	65	35		45-50	Cv	18	82
	50-55		61	39		50-55		22	78

* Sand fraction >0.063 mm

* Clay and silt fraction <0.063 mm

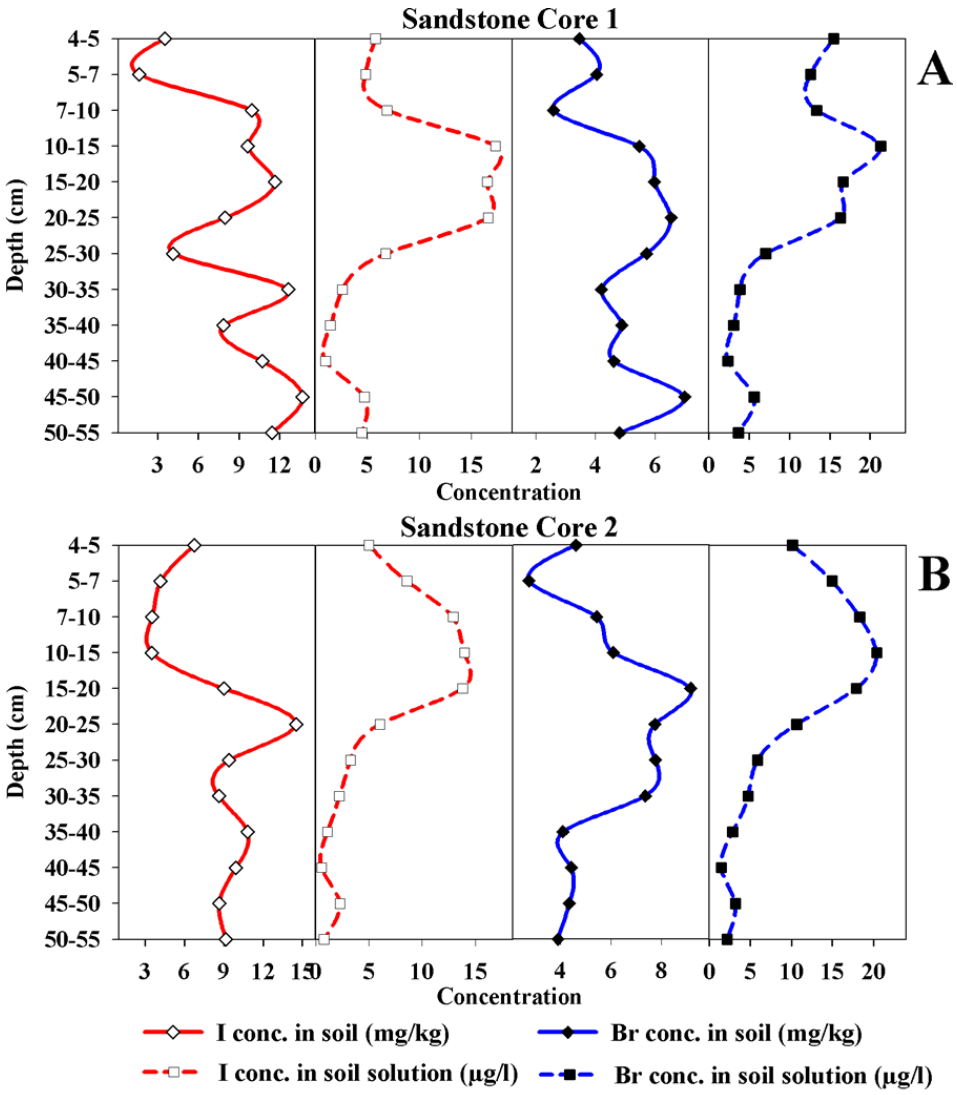

Fig. 31. Iodine and bromine in soils and soil solutions of the two Sandstone site cores.

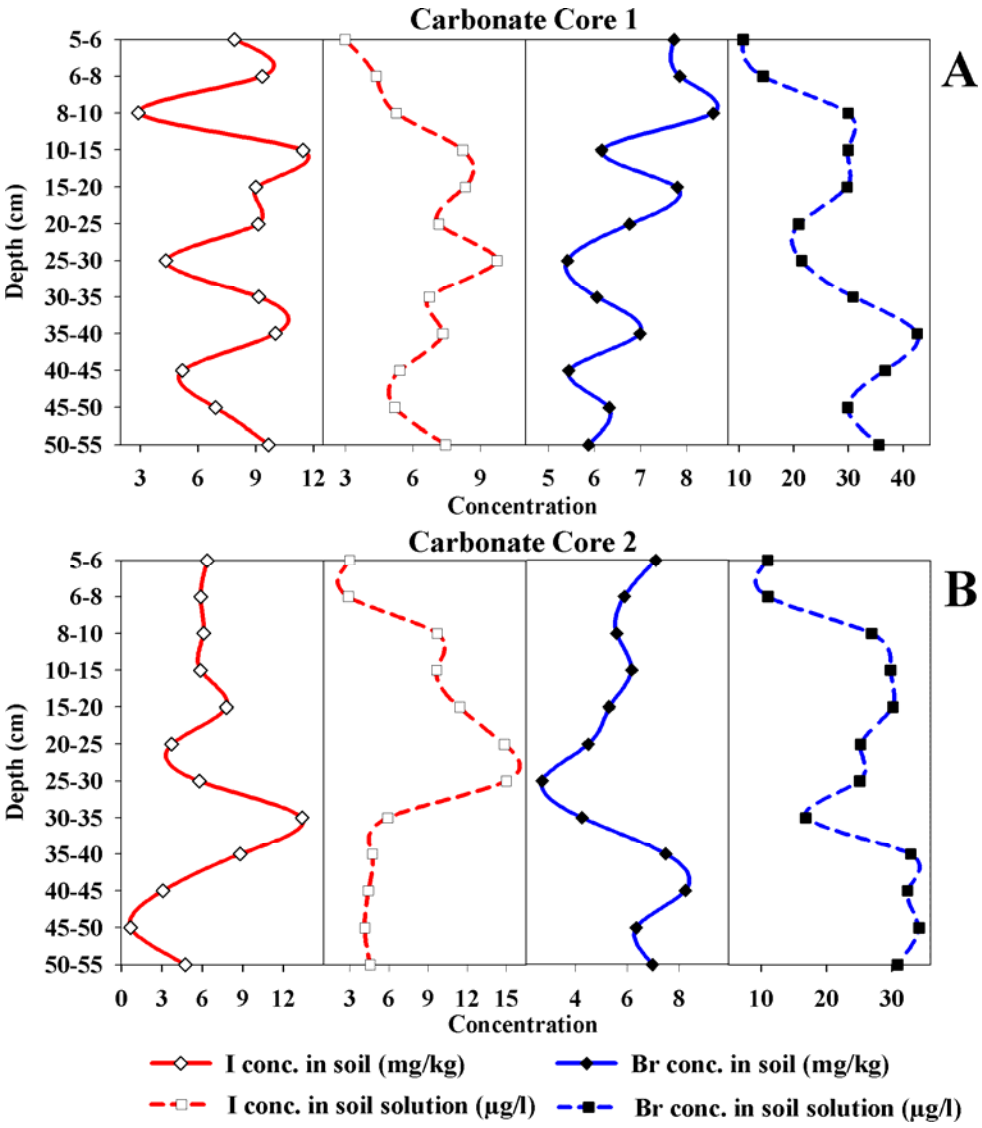

Fig. 32. Iodine and bromine in soils and soil solutions of the two Carbonate site cores.

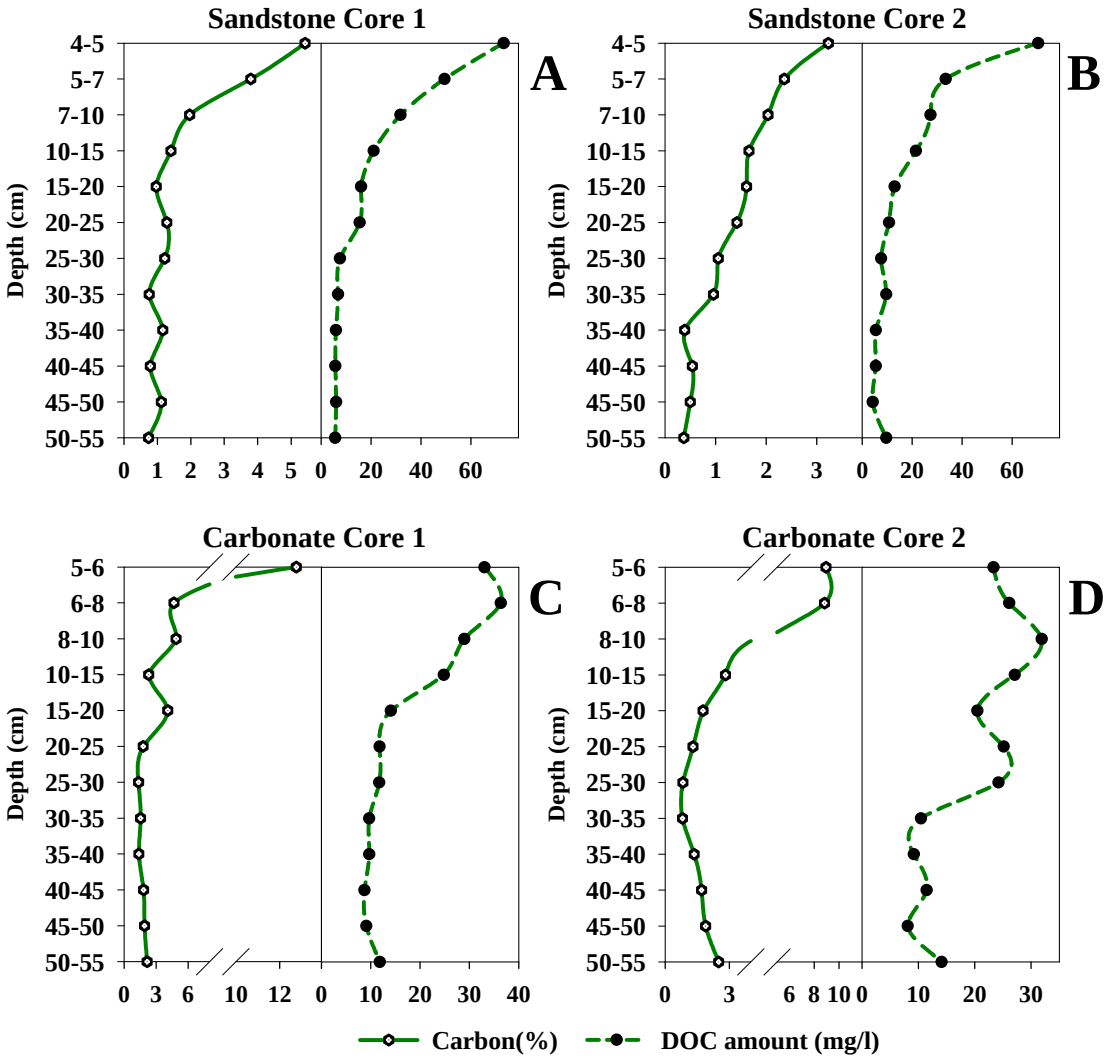

Fig. 33. Total carbon content in soil and dissolved organic carbon concentrations in soil solution. A, B) Sandstone site cores, C, D) Carbonate site cores.

3.4.5. Halogens in soil solutions

Total iodine and bromine content of a soil depends, in part, on the quantities supplied to the soil by the weathering of primary minerals and accessions for the atmosphere, and in part on the ability of the soil to retain it (Whitehead, 1973b).

Versatile formation and release processes are affecting the distribution pattern of halogens in soils, and involve oxidation, reduction, sorption, desorption and specific linkage to soil constituents. These reactions will govern the extent to which halogens are retained, leached and their potential to volatilize (Whitehead, 1973b; Sheppard et al., 1992). In order to quantify the net results of these effects, halogen concentrations in soil solution were measured.

The distribution of iodine and bromine in soil solutions of the Sandstone site are shown in Fig. 31A, B. Average dissolved iodine concentration in section 4-5 cm is 5.4 ± 0.6 µg/l and increases up to a concentration of 15.6 ± 2.3 µg/l in section 10-15cm, which is the end of the Ao horizon. Again, at the beginning of the Bt horizon (15-20 cm) the iodine concentration is high (15 ± 2 µg/l). The dissolved iodine concentration in deeper sections decreases, but again an increase occurs in section 45-50 cm and is related to the transition to the Cv horizon. As already mentioned in section 3.4.4.

Total average dissolved bromine concentrations in the Sandstone site cores is 12 ± 3.8 µg/l in the first section (4-5 cm) and increases by 61% to a concentration of 21 ± 0.6 µg/l in section 10-15 cm which is the maximum concentration in the examined soil profiles and represents the end of the Ao horizon. The dissolved bromine concentration in deeper sections decreases to a concentration of 2.9 ± 1 µg/l. Noticeably an influence of the Cv horizon is shown in section 45-50 cm were a minor increase is noticed. The dissolved organic matter (DOC) pattern shows a decrease as function of the profile depth.

Iodine and bromine distribution at the Carbonate site are shown in Fig. 32A, B. The iodine and bromine distribution patterns between the cores are less diverse compared to their distribution patterns in soil. Average dissolved iodine in the first soil section (5-6 cm) is 3 µg/l and increases up to a concentration of 11 ± 5.4 µg/l in section 20-25 cm which is the end of the Ah horizon. Average dissolved bromine in the first soil section (5-6 cm) is 11 ± 0.2 µg/l and increases up to a concentration of 23 ± 2.5 µg/l in section 20-25 cm (end of the Ah horizon). Dissolved bromine concentrations in deeper sections are higher compared to upper sections and at the lowest examined section (50-55 cm) the bromine concentration is 33 ± 3.3 µg/l.

The iodine and bromine distribution patterns in soil solutions of each core at both sites are similar in the topsoil sections where an organic layer is present, by this we can point out that the behavior of halogens (sorption and desorption) in soil are related to soil organic matter (SOM) and an accumulation is occurring in this section. In addition, the concentration of halogens at both sites are higher compared to their rain concentrations, indicating that the precipitated halogens are adsorbed by the SOM, integrated in the existing soil halogen pool and moved through the soil column with the dissolved organic carbon (DOC).

Average bromine concentration from the Cv horizon (section 45-55 cm) was compared to the average bromine concentration at the equivalent sandstone site sections. The calculation reveals that the bromine concentration in the Carbonate site is about ten times higher (9.4 ± 3). Again, emphasizing the parent material influence. A similar effect can also be observed for iodine, although to a lesser extent. The fact that carbonaceous material is easily weathered, leads to elevated clay and silt content in these soils (Gerzabek et al., 1999), phenomena that was noticed

also in the examined site and can be seen in the grain size analysis. Nevertheless, atmospheric deposition remains the main source for halogens at both sites.

The halogen percentage release by water was calculated by dividing the total amount of halogens in the leaching solution (10 ml Millipore water) with the total amount of the halogens in the soil (1 g dry weight). The halogen percentage release for the Sandstone site is shown in Fig. 34. The results show that the release patterns are similar for the examined cores. In the Ao horizon (until a depth of 15cm) the release is the highest throughout the profile, iodine and bromine releases are 2% ± 0.7 and 3.9% ± 0.5, respectively (average of the two profiles). A decrease in the percentage released is noticed for the Bt horizons (iodine and bromine release are 1.2% ± 0.2 and 1.8% ± 0.7, respectively). Followed by another decrease in both the Bv and Cv horizons, as the halogens are exhibiting a low release. The iodine and bromine percentage release in these horizons are 0.2% ± 0.1 and 0.7% ± 0.1, respectively. The data indicate that more halogens are released in soil organic horizons compared to mineral horizons reflecting their mobility potential when interacting with water. These results point toward the nature of the binding and suggest that only the weakly bound halogens/organohalogens and the free organohalogens are dissolved by water. In mineral horizons at this site the halogens release is low, reflecting the low concentration founds in soil, which can indicate different desorption mechanism and kinetics compared to the organic horizon properties.

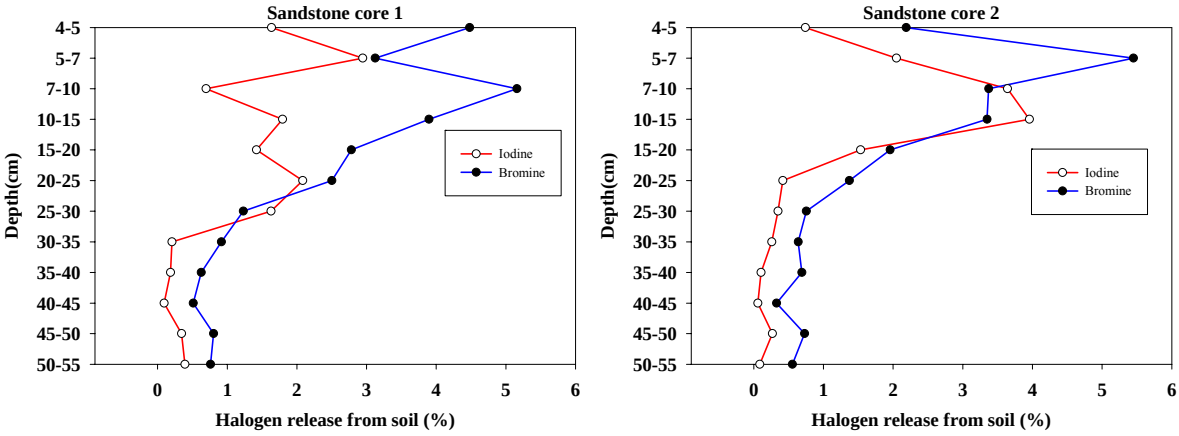

Fig. 34. Halogen percentage release at Sandstone site.

The same calculation was performed for the iodine and bromine concentration at the Carbonate site and is shown in Fig. 35. The data show some discrepancies which are related to the different patterns between the examined cores (see Fig. 32). Due to the discrepancies the two cores can not be compared and have to be treated separately. Nevertheless, we notice an increase in the release of iodine and bromine at the upper horizon (Ao) as depth increase. Initially, iodine and

bromine release is (0.4% ± 0.1 and 1.5% ± 0.1, respectively) and increases until the end of the organic horizon (1.7% ± 0.15 and 4.2% ± 0.9, respectively) again showing the mobility of the halogens within the soil profile. This behavior indicates that within this layer the halogens are bound to soil organic matter and as the degradation of the organic matter increases with soil depth an increase in the halogen release is observed. In the second horizon (Ah, 10-25 cm), the first core exhibits an increase in the percentage release while the second core shows a decrease. In the third horizon (Bv, 25-45 cm) the same antagonistic pattern occurs but the differences are narrowing down. Iodine release percentage is 1.2% ± 0.85 while bromine release percentage is 5.4% ± 1. In the forth horizon (Cv, 45-55 cm) the trend continues, iodine release percentage is 2.2% ± 1.8 while bromine release percentage is 5.2%.

The halogens percentage release at the mineral soil horizons (Bv and Cv) shows that the minerals containing the halogens are releasing them. The carbonate content in this section (30-55 cm) increases up to 10% (Table 24). The bromine percentage release indicates that a vertical migration of this element might occur in higher rates compared to iodine.

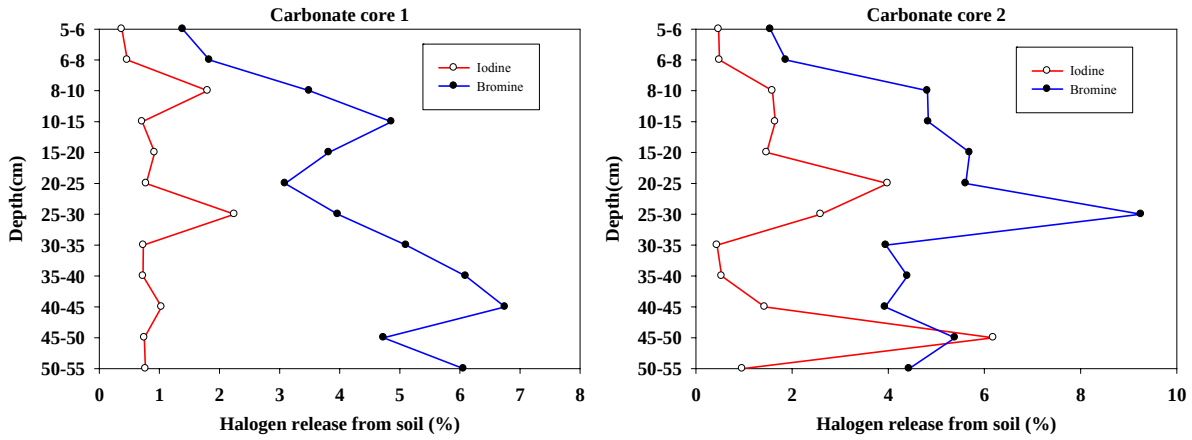

Fig. 35. Halogen percentage release at Carbonate site.

3.4.6. Halogens speciation in soil solutions

Halogen species determination in soil is of importance since both organic and inorganic halogen species interact with soil compounds. The presence of organohalogens in soil is a result of halogen reactions with the large pool of organic compounds (some of them are water soluble) in the soil, resulting in versatile compounds with different properties. The organohalogens vary in their stability, and some of them are volatile, can react with additional compounds and even be used as nutrient source for soil organisms.

Unfortunately, the speciation knowledge of organoiodine and organobromine in soil is poorly studied, limiting the knowledge about their specific properties.

Yamada et al., (1999) demonstrated that iodine in soil can exist in four forms: organic iodine bound to humic acids, organic iodine bound to fulvic acids, inorganic iodide, and inorganic iodate. Biester el al., (2004) showed that in Chilean histosoils (peat bogs) up to 91% of bromine and 81% of iodine are present in an organic form.

Fig. 36 shows the total iodine and bromine as well as their organic species (in percentage) at both locations (measured in soil solution). An examination of the organic species was performed in soil solution of both the sites.

At the Sandstone site (Fig. 36A, B) the iodine species in the Ao horizon (section 4-15 cm) are mostly organic (93% ± 3.7). The percentage of organic iodine decreases by 15% from the end of the organic layer until the end of the examined core (50-55 cm). A decrease in the iodine organic fraction is occurring at section 25-30 cm and represents the changes due to horizon transition. Another decrease occurs again at the beginning of the Cv horizon. The presence of organobromine in soil solution decreases by 37% from the end of the A horizon until a depth of 40-45 cm (end of the Bv horizon) which is followed again by an increase.

The change of the species to inorganic form occurs both for iodine and bromine and can be explained by the transition between the soil horizons but can also be a result of biological activities. The soils of the examined area possess high bioactivity and the halogens speciation can be changed due to chemical and biological process in tree rhizosphere (e.g. reaction with organic acid in root exudates, pH changes) and even by local microbial consumption of organic compounds.

Halogen speciation for the Carbonate site is shown in Fig. 36C, D. Iodine in section 5-10 cm (Ao horizon) is completely organic. A shifting towards an inorganic fraction occurs very slowly as the depth increases. In average the iodine organic percentage average is 96.3% ± 3.9.

The average of organic bromine percentage in the soil solution at the first examined section (5-6 cm) is 71.6% ± 8.6 and increases to 92.3% ± 5.4 at section 20-25cm. This increase occurs at the end of the Ah horizon emphasizing the effect of horizon properties, mobility and organic matter on organobromine. In the mineral horizons the bromine organic percentage decreases as a result of the influence of the parent material on the soil. The carbonate bedrock is releasing inorganic bromine while it is weathered. The total average of bromine in the examined cores is 66% ± 14 which is low compared to the Sandstone site emphasizing the source influence on the soil.

The halogen species in the soil determine if they will be taken up by the Atlantic beech (*Fagus Sylvatica*) which is the dominate vegetation in the sites, iodide or bromide are the preferred forms. Nevertheless, an overview of the mature leaves content from both of the sites (similar

date) (Table 21) shows that the bromine content is higher in the Sandstone site while iodine is higher in the tree leaves from the Carbonate site. The results indicate that the uptake of bromine and iodine might occur in a deeper section than the examined profiles.

Examination of the results reveals that in presence of soil organic matter the organohalogens are the dominant fraction in soil. Organohalogens are formed by adsorption/affinity to humic acids as well as by ageing and degrading of organic matter and by microorganisms and fungi that reside in the soil. Furthermore, Rädlinger and Heumann (2000) showed that microorganisms enhance the transformation of inorganic iodine into humic acid/iodine species. The importance of the organic matter fraction in the soil as a sorbing agent for iodine has been shown also in prior works (Whitehead, 1978; Sheppard and Thibault, 1992). In lower sections of the profile the organic fraction decreases. The influence of the parent material at the Carbonate site is observed again, when the amount of inorganic bromine is higher compared to upper sections and to the equivalent Sandstone site sections.

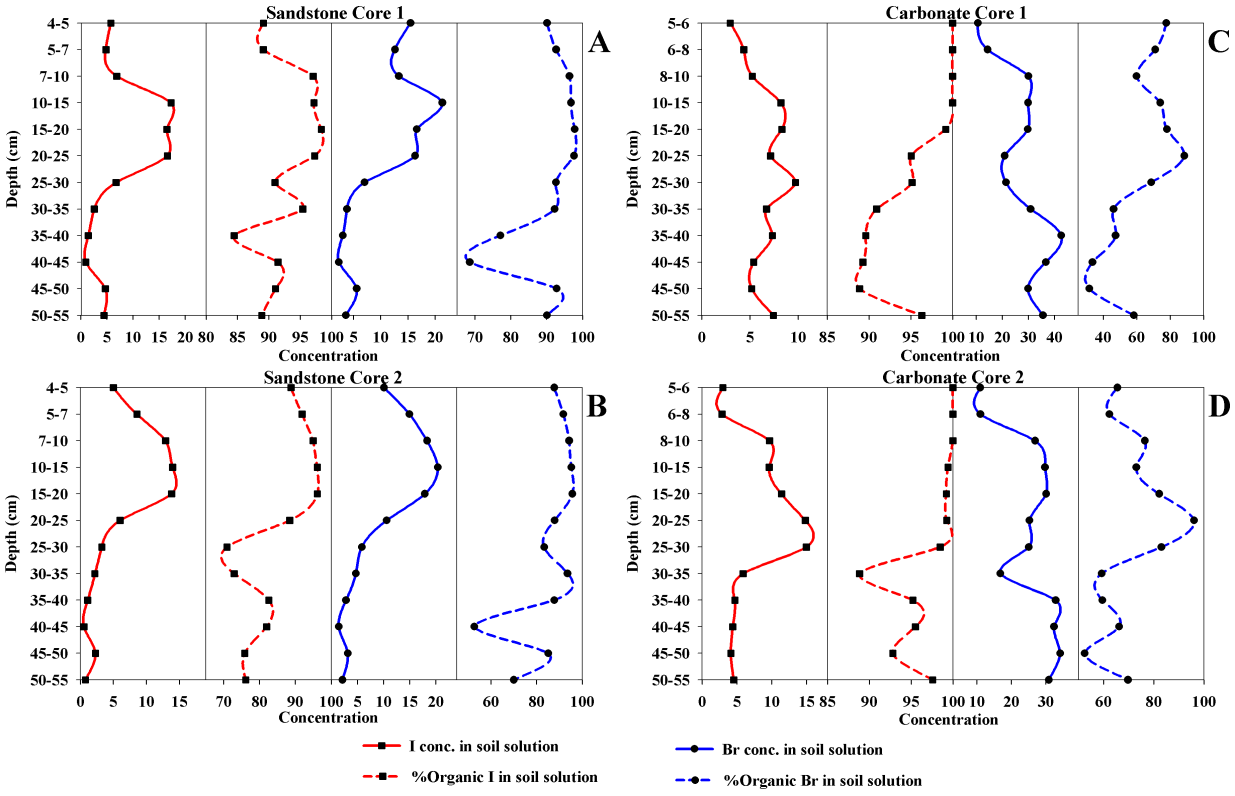

Fig. 36. Distribution of dissolved organic iodine/bromine fractions in soil solution.
A, B) Sandstone site cores, C, D) Carbonate site cores.

3.4.7. Soil properties

The soil pH data are shown in Table 23 reflecting the different soil origins. In the Sandstone location the soil is more acid compared to the Carbonate site. It is known that even 1% of carbonate in a soil can dominate the course of soil development because this amount is sufficient to raise the pH to a value above neutrality and sustain a high level of biological activity (FitzPatrick, 1980). The measurement of the carbonate contents (Table 24) was performed using the carbonate bomb technique. The technique showed carbonate presence only in the lower section of the Carbonate site, reflecting the carbonate bedrock. As expected no carbonate was detected at the Sandstone site. It is important to take under consideration that carbonate bomb detection limit is 5% for 0.76g of soil. In order to achieve the concentrations described in Table 24 up to 3.5g were used.

Table 23. Soil pH data.

	Sandstone site			Carbonate site	
	Core 1	Core 2		Core 1	Core 2
Depth (cm)	pH		Depth (cm)	pH	
4-5	4.3	4.3	5-6	7.3	7.6
5-7	4.2	4.5	6-8	7.2	7.3
7-10	4.45	4.55	8-10	7.5	7.25
10-15	5	4.8	10-15	6.9	7.2
15-20	5	5	15-20	7	7.2
20-25	4.9	4.8	20-25	7.6	7
25-30	4.7	4.7	25-30	7.6	6.9
30-35	4.6	4.7	30-35	7.6	7.6
35-40	4.7	4.6	35-40	7.5	7.5
40-45	4.6	4.6	40-45	7.5	7.4
45-50	4.7	4.6	45-50	7.6	7.7
50-55	4.8	4.6	50-55	7.6	7.6

Table 24. Soils carbonate content.

	Sandstone site			Carbonate site	
	Core 1	Core 2		Core 1	Core 2
Depth (cm)	% Carbonate		Depth (cm)	% Carbonate	
4-5	n.d.	n.d.	5-6	n.d.	n.d.
5-7	n.d.	n.d.	6-8	n.d.	n.d.
7-10	n.d.	n.d.	8-10	n.d.	n.d.
10-15	n.d.	n.d.	10-15	n.d.	n.d.
15-20	n.d.	n.d.	15-20	n.d.	n.d.
20-25	n.d.	n.d.	20-25	n.d.	n.d.
25-30	n.d.	n.d.	25-30	n.d.	n.d.
30-35	n.d.	n.d.	30-35	1.6	1.0
35-40	n.d.	n.d.	35-40	2.7	2.7
40-45	n.d.	n.d.	40-45	5.0	4.7
45-50	n.d.	n.d.	45-50	6.5	7.2
50-55	n.d.	n.d.	50-55	8.0	10.0

*n.d. – not detected, Detection limit 1%

3.4.8. Halogens mass balance in the forest sites

Compiling all the data shown in this section allows a calculation which will provide additional information on the distribution and cycling of halogens in the environment. The calculation is based on the averages between the sites.

3.4.8.1. Bromine mass balance in the forest sites

Bromine was calculated first and the results are as followed:

Bromine in leaves: The average leaf biomass of *Fagus Sylvatica* is 3.5 t/ha·yr (350 g/m^2·yr) (Schulze, 2000). The average bromine content in leaves is 1 mg/kg and since all the leaves are shading in autumn, total bromine flux is **$3.5 \cdot 10^{-4}$ g/m^2·yr**.

Bromine in leaf litter: The ages of the trees are important in order to estimate the amount of litter. Lebret et al., (2001) showed that sapling trees (27 years old) and 83 years old tree are

producing similar litter (3.8 and 3.9 t/ha·yr, respectively). Since the sampling site trees are estimated to be aged in this time scale an average of 3.85 t/ha·yr was used. The number is higher compared to the leaf biomass since the litter also contains other plants parts (e.g. twigs). Average bromine content for the three layers examined was 4.5 mg/kg (as described in section 2.4.2). The calculation results that the litter bromine flux is **$1.7 \cdot 10^{-3}$ g/m^2·yr**.

Bromine in rainfall: The bromine flux is **$1.9 \cdot 10^{-3}$ g/m^2·yr**.

Overall bromine input: Bromine in leaves and rainfall are the input at this examined ecosystem and are calculated as **$2.25 \cdot 10^{-3}$ g/m^2·yr**.

Bromine in soil: The average bromine content in the examined sites is: 5.8 mg/kg, the density of the soil is assumed to be 1600 kg/m^3 (Schöler et al., 2003b). The examined area is 0.5 m^3 (1 m^2, 0.5 m depth). The calculation results: **4.64 g**.

Except for bromine content in soil all the results are per annum, creating an obstacle to perform a balance. Nevertheless, the calculation above indicate that 0.075% of the bromine in the soil stored in the leaves, this calculation does not include how much is stored in the roots, twigs and trunk (based on calculation with 1 m^2). The amount in the litter is 5 times higher, indicating an enrichment process. The overall bromine input flux value (**$2.25 \cdot 10^{-3}$ g/m^2·yr)** is higher then the litter flux **($1.7 \cdot 10^{-3}$ g/m^2·yr),** this suggests that atmospheric input is an important source for bromine in the litter but a calculation also shows that in the litter there is a bromine loss (24.4%). Pervious experiments showed that under laboratory conditions up to 12.9% ± 6.1 of the bromine can be volatilized (92 days of decomposition). The dissimilarity can be a result of different decomposition times. Although no field measurements are known for the bromine emission in this forest ecosystem and with respect to the 12.9% ± 6.1 that were liberated under laboratory conditions, this calculation emphasizes that the bromine activity in terrestrial ecosystems is underestimated in the global balance of methyl bromide. Nevertheless, the bromine fraction that is volatilized under field conditions can be influenced by various parameters such as, litter quality of *Fagus Sylvatica* leaves, microorganisms` (fungi and bacteria) presence and activity, and even microclimatic conditions (temperature, humidity, etc).

3.4.8.2. Iodine mass balance in the forest sites

The same calculation was applied on iodine and the results are as follow:

Iodine in leaves: Total iodine content in leaves is 2 mg/kg, resulting a flux of **$7 \cdot 10^{-4}$ g/m^2·yr**.

Iodine in leaf litter: Leaf litter contain 6.9 mg/kg, total iodine flux of litter is **$2.65 \cdot 10^{-3}$ g/m^2·yr**.

Iodine in rainfall: Rainfall total iodine flux is **$3 \cdot 10^{-4}$ g/m^2·yr**.

Overall iodine input: Iodine in leaves and rainfall are the input at this examined ecosystem and are calculated as **$1 \cdot 10^{-3}$ g/m^2·yr**.

Iodine in soil: Total iodine content in soil is **6.16 g**.

Unlike the bromine, the iodine results contain uncertainties since the amount in the leaves is elevated. Examination of halogen uptake by *Lolium multiflorum* indicates that the iodine uptake is much lower compared to bromine uptake. In addition, two out of the six samples were below the detection limit and a single sample had a relatively high concentration of 4.3 mg/kg (as shown in Table 21).

As expected the amount of iodine in rain was low by a factor of 10. The sum of the amount of iodine in rainfall and leaves **($1 \cdot 10^{-3}$ g/yr)** is lower compared to the amount in leaf litter **($2.65 \cdot 10^{-3}$ g/yr).** This indicates that iodine is not released as efficiently as bromine, similar to the results of *Lolium multiflorum* decomposition (section 3.2.2.5).

4. Conclusion

In this work some aspects of iodine and bromine were investigated in three compartments: plants, decomposed material and soil. The conclusions are summarized according to the compartments.

Plants:

- Iodine uptake by *Lolium multiflorum* plants is lower compared to bromine uptake. Possibly reflecting different uptake mechanisms.
- Bromine might interfere with nitrogen and hydrogen content in the plant, an investigation with higher concentrations is necessary.

Decomposed material:

- The halogen contents can remain, leach or volatilize from decay plant material during decomposition process.
- Maximum release of soluble halogens from *Lolium multiflorum* occurs within three weeks form the starting of the experiments, while *Fagus Sylvatica* leaves decompose slowly. Emphasizing the importance of the litter quality.
- The results imply that plants store bromine in inorganic forms while iodine is also stored in organic forms.
- The halogens transition between inorganic/organic forms in the leached solution is related to their initial form in the plant but can also be influenced by decomposing organisms.
- Different release rates of iodine and bromine from examined decomposed plants were observed.
- Plant decomposition processes can be a source for volatile halogens in an ecosystem.

Forest ecosystem:

- Iodine and bromine tend to be affected similarly by soil formation processes.
- An accumulation of halogens is noticed in organic soil horizons.
- In organic rich soils halogens bind to organic matter, resulting organohalogens.
- In topsoil, organohalogens are the dominant fraction.
- In subsoil horizons poor in organic matter the organohalogens concentrations are decreasing.

- Atmospheric deposition is the main source for halogens in the terrestrial environment. In some areas an additional influence can be from parent material
- An enrichment of halogens is noticed in leaf litter.
- Up to 24.4% from the bromine input to the system is lost, possible as a volatile form.

The results reveal that some of the halogen complexities are mainly related to biogenic processes. Furthermore iodine and bromine might not behave the same in all the aspects of the terrestrial environment. Implementing the results of one halogen to the other should be carried out with extreme caution.

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6. Appendix

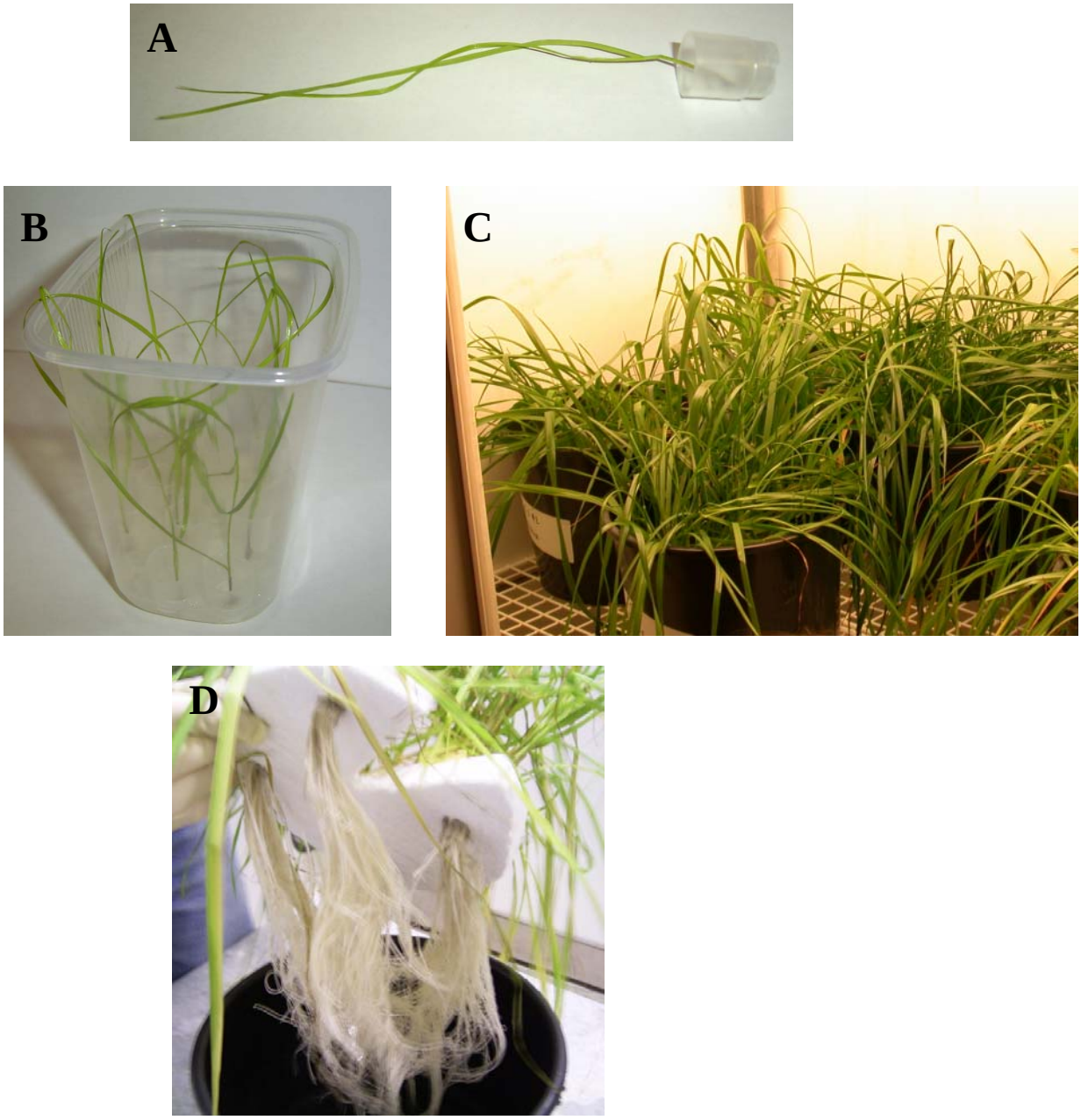

Fig. 37. Culture setup pictures: A) 3 weeks Seedling, 2) Growth box, 3) *Lolium multiflorum* plants in growth chamber, D) *Lolium multiflorum* root system.

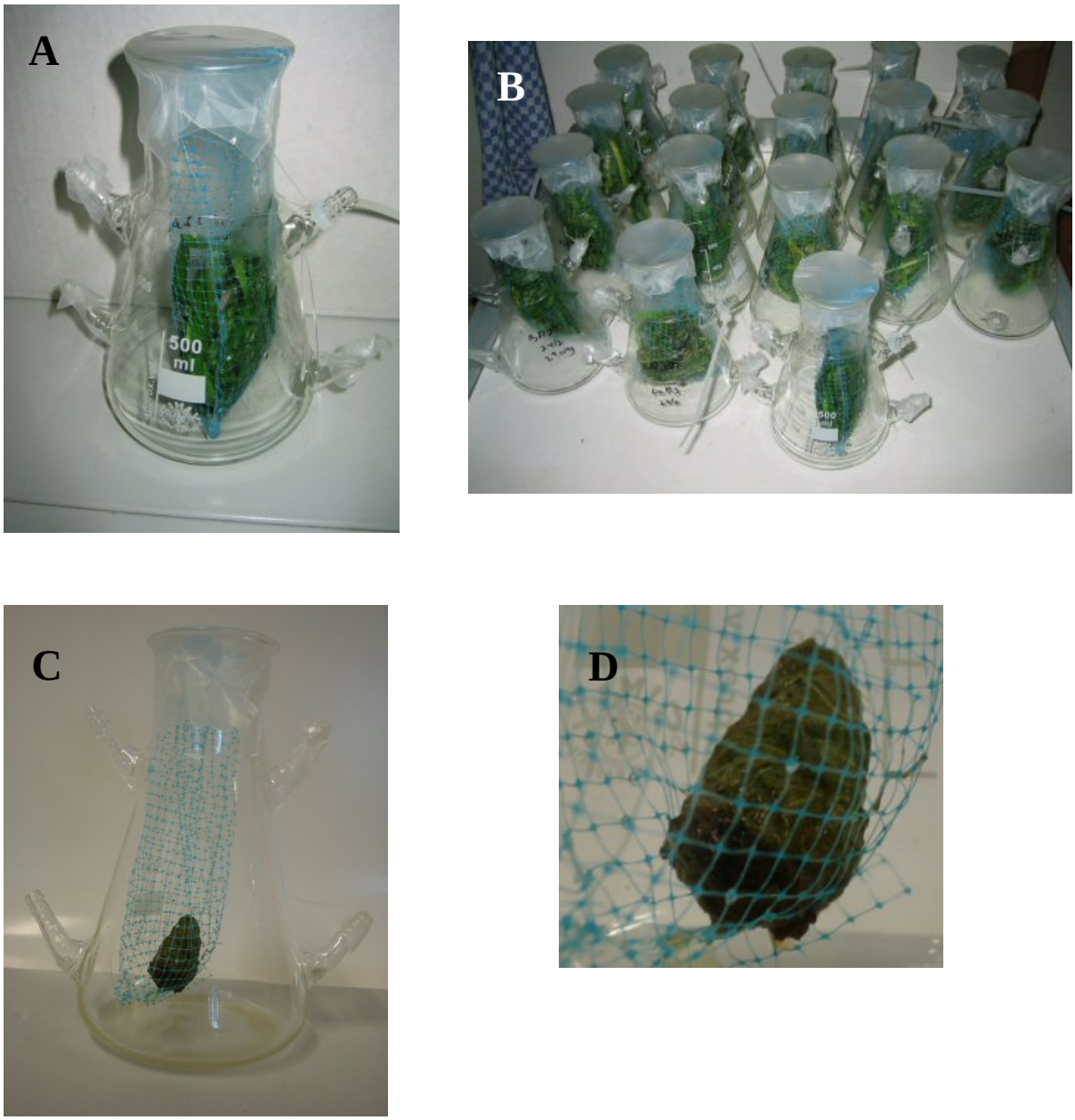

Fig. 38. Decomposition apparatus pictures: A) Decomposition apparatus at the beginning of the experiment, B) Setup of decomposition apparatus, C) Decomposition at the experiment end, D) Closer look of the decomposed debris after 3 months.

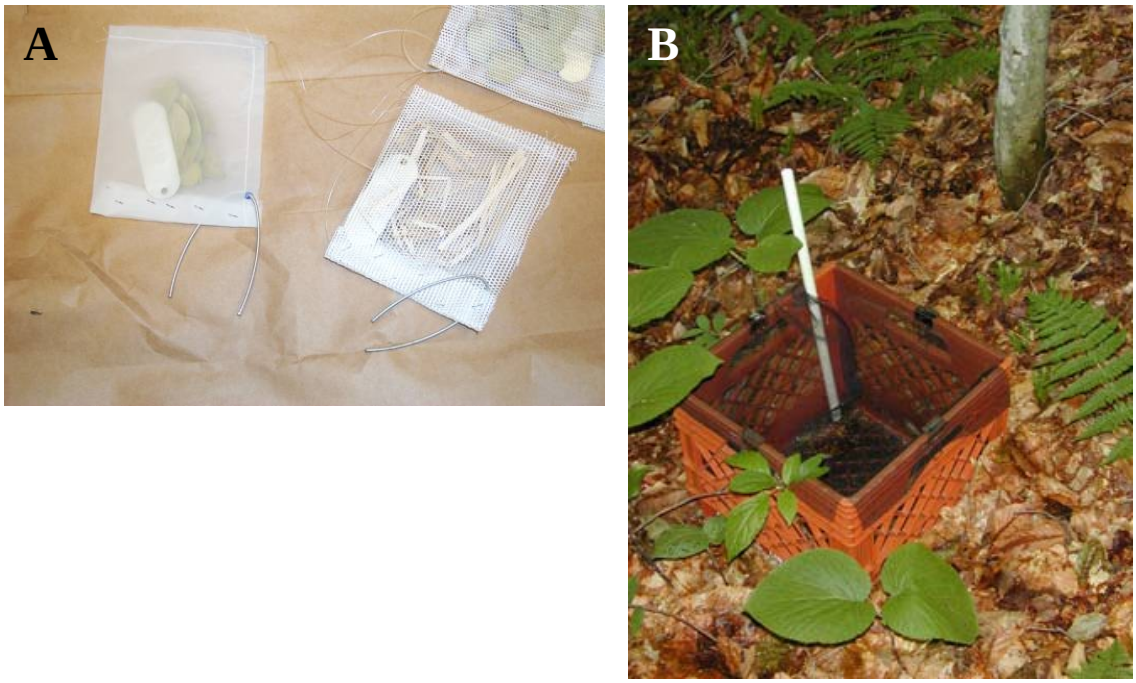

Fig. 39. Typical decomposition apparatus: A) Litter bag, B) Litter basket.

Table 25. Average bromine enriched plant water percentage.

Plant code	Total sample weight (g)		%Water
	Before freeze dryer	After freeze dryer	
Bcon1A	50	11.6	76.7
Bcon1B	11.5	4.1	64.4
Bcon2A	39.4	11.2	71.6
Bcon2B	47.5	11.5	75.7
Average	37.1±17.7	9.6±3.7	72.1±5.6
Br11A	32.5	11.2	65.6
Br11B	32.4	10.6	67.4
Br12A	47.3	11.1	76.5
Br12B	32.6	10.4	68.2
Average	36.2±7.4	10.8±0.4	69.4±4.8
Br21A	47.1	11.3	76.1
Br21B	55.2	12.1	78.2
Br22A	30.4	10.2	66.4
Br22B	29.1	10.3	64.7
Average	40.5±2.8	11±0.9	71.3±6.7
Br31A	48.2	11.6	75.9
Br31B	37.8	4.6	87.8
Br32A	18	4.5	74.9
Br32B	45.4	10.2	77.5
Average	37.4±13.6	7.7±3.7	79±6
Average - all samples	37. 8±12.1	9.8±2.7	73±6

Table 26. Bromine enriched plants decomposition - bromine release data.

Control plants

Day	Bcon1A Total Br (µg/l)	Bcon1A stdev	Bcon1A Inorganic Br (µg/l)	Bcon1A Organic Br(µg/l)	Bcon1A %Inorganic Br	Bcon1A %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	3.7	n.d.	3.7	n.d.	100	n.d.
8	19.6	0.8	0.4	19.2	2.0	98.0
12	203	9.3	3.4	199	1.7	98.3
15	105	3.7	15.9	88.9	15.2	84.8
19	63.6	2.1	6.3	57.3	9.9	90.1
22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
29	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
50	2.5	0.1	0.3	2.2	12.8	87.2
69	2.0	0.0	0.3	1.6	16.6	83.4
84	2.2	0.1	0.7	1.5	32.5	67.5
97	1.1	0.1	0.3	0.8	25.5	74.5
111	1.2	0.1	0.4	0.8	30.6	69.4
120	2.4	0.2	0.5	1.9	20.7	79.3

Day	Bcon1B Total Br (µg/l)	Bcon1B stdev	Bcon1B Inorganic Br (µg/l)	Bcon1B Organic Br (µg/l)	Bcon1B %Inorganic Br	Bcon1B %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	2.2	0.0	2.2	n.d.	100	n.d.
8	6.6	0.3	6.6	n.d.	100	n.d.
12	17.9	4.5	6.6	11.3	37.0	63.0
15	69.5	0.8	1.9	67.5	2.8	97.2
19	54.5	0.8	1.6	53.0	2.8	97.2
22	10.6	0.8	10.6	n.d.	100	n.d.
26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
29	3.3	0.5	0.4	2.9	12.5	87.5
34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
50	2.0	0.0	0.2	1.9	8.6	91.5
69	1.1	0.1	0.1	1.0	10.7	89.3
84	1.4	0.0	0.2	1.2	13.7	86.3
97	0.9	0.1	0.1	0.8	13.5	86.5
111	2.0	0.1	0.6	1.4	32.3	67.7
120	1.4	0.1	0.4	1.0	29.1	70.9

Day	Bcon2A Total Br (µg/l)	Bcon2A stdev	Bcon2A Inorganic Br (µg/l)	Bcon2A Organic Br (µg/l)	Bcon2A %Inorganic Br	Bcon2A %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	2.6	n.d.	2.6	n.d.	100	n.d.
8	0.2	n.d.	0.2	n.d.	100	n.d.
12	24.3	7.2	8.7	15.6	35.7	64.4
15	104	3.4	8.2	95.7	7.9	92.2
19	82.5	2.4	2.8	79.7	3.4	96.6
22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
29	1.9	0.0	1.9	n.d.	100	n.d.
34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
50	4.7	0.1	1.0	3.7	21.5	78.5
69	2.5	0.1	0.6	2.0	21.8	78.2
84	1.8	0.0	0.2	1.6	8.3	91.7
97	0.6	0.1	0.1	0.5	22.0	78.1
111	2.5	0.1	0.8	1.7	33.4	66.6
120	2.4	0.2	0.8	1.6	34.2	65.8

Day	Bcon2B Total Br (µg/l)	Bcon2B stdev	Bcon2B Inorganic Br (µg/l)	Bcon2B Organic Br (µg/l)	Bcon2B %Inorganic Br	Bcon2B %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	31.9	0.9	31.9	n.d.	100	n.d.
8	3.6	32.0	3.6	n.d.	100	n.d.
12	4.6	0.0	4.6	n.d.	100	n.d.
15	93.2	2.1	1.7	91.5	1.8	98.2
19	65.4	2.4	1.4	64.1	2.1	97.9
22	91.0	3.2	1.6	89.4	1.7	98.3
26	9.1	4.7	1.0	8.1	11.2	88.8
29	10.2	2.8	1.0	9.2	9.7	90.3
34	4.1	0.9	2.9	1.3	69.1	30.9
40	15.2	1.5	1.7	13.5	11.2	88.8
50	7.2	0.1	0.8	6.4	11.3	88.7
69	5.9	0.1	1.4	4.5	23.7	76.3
84	7.4	0.1	1.6	5.8	21.2	78.8
97	4.6	0.1	1.2	3.4	26.0	74.0
111	2.1	0.1	0.8	1.3	36.6	63.4
120	1.0	0.2	0.3	0.7	28.8	71.2

0.05 mg/l bromine enriched plants

Day	Br11A Total Br (µg/l)	Br11A stdev	Br11A Inorganic Br (µg/l)	Br11A Organic Br (µg/l)	Br11A %Inorganic Br	Br11A %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	12.5	0.2	12.5	n.d.	100	n.d.
8	176	1.3	176	n.d.	100	n.d.
12	353	4.1	353	n.d.	100	n.d.
15	82.2	0.7	0.2	82.2	n.d.	100
19	111	2.1	58.6	51.9	53.0	47.0
22	57.5	13.3	48.2	9.3	83.8	16.2
26	87.7	3.4	87.7	n.d.	100	n.d.
29	146	2.6	128	18.1	87.6	12.4
34	230	1.1	230	n.d.	100	n.d.
40	210	3.4	183	26.8	87.2	12.8
50	201	4.0	161	40.6	79.8	20.2
69	192	3.4	145	47.1	75.4	24.6
84	122	1.3	93.4	27.8	77.0	23.0
97	64.0	0.6	50.0	14.0	78.2	21.8
111	39.5	1.6	30.7	8.8	77.8	22.3
120	21.9	1.3	16.5	5.4	75.5	24.5

Day	Br11B Total Br (µg/l)	Br11B stdev	Br11B Inorganic Br (µg/l)	Br11B Organic Br (µg/l)	Br11B %Inorganic Br	Br11B %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	12.6	0.0	12.6	n.d.	100	n.d.
8	307	2.4	307	n.d.	100	n.d.
12	386	3.2	386	n.d.	100	n.d.
15	112	1.9	82.9	28.8	74.2	25.8
19	71.0	1.9	26.1	44.9	36.8	63.2
22	12.4	1.5	12.4	n.d.	100	n.d.
26	22.5	1.7	22.5	n.d.	100	n.d.
29	26.9	1.2	19.8	7.1	73.7	26.3
34	46.3	1.1	41.5	4.8	89.7	10.3
40	41.0	2.9	41.0	n.d.	100	n.d.
50	80.6	0.5	67.3	13.3	83.6	16.4
69	81.6	0.5	70.8	10.8	86.8	13.2
84	40.0	0.4	32.7	7.3	81.7	18.3
97	19.8	0.4	15.2	4.5	77.2	22.8
111	12.9	0.3	10.7	2.2	82.7	17.3
120	8.8	0.4	6.3	2.5	71.8	28.2

Day	Br12A Total Br (µg/l)	Br12A stdev	Br12A Inorganic Br (µg/l)	Br12A Organic Br (µg/l)	Br12A %Inorganic Br	Br12A %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	92.1	0.4	92.1	n.d.	100	n.d.
8	855	4.8	855	n.d.	100	n.d.
12	1042	6.5	1042	n.d.	100	n.d.
15	395	7.6	297	98.2	75.2	24.9
19	267	5.2	178	88.6	66.8	33.2
22	430	16.9	164	267	38.0	62.0
26	185	3.4	177	7.7	95.9	4.1
29	42.6	0.7	1.9	42.6	n.d.	100
34	118	0.4	118	n.d.	100	n.d.
40	85.1	2.7	85.1	n.d.	100	n.d.
50	56.4	0.3	46.2	10.2	81.9	18.1
69	39.8	0.2	13.8	26.1	34.6	65.5
84	23.7	0.2	4.7	19.0	19.8	80.2
97	16.0	0.2	2.2	13.8	14.0	86.1
111	7.7	0.2	1.4	6.3	18.0	82.1
120	13.5	0.7	3.2	10.3	23.7	76.3

Day	Br12B Total Br (µg/l)	Br12B stdev	Br12B Inorganic Br (µg/l)	Br12B Organic Br (µg/l)	Br12B %Inorganic Br	Br12B %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	81.1	1.4	81.1	n.d.	100	n.d.
8	392	2.7	392	n.d.	100	n.d.
12	505	19.6	505	n.d.	100	n.d.
15	221	9.7	148	73.1	67.0	33.1
19	139	5.3	80.1	58.5	57.8	42.2
22	87.0	5.7	46.3	40.8	53.2	46.8
26	48.6	3.8	48.6	n.d.	100	n.d.
29	73.6	0.7	41.2	32.4	56.0	44.0
34	27.8	0.7	27.8	n.d.	100	n.d.
40	36.1	2.3	36.1	n.d.	100	n.d.
50	30.5	0.4	23.6	6.9	77.4	22.7
69	15.8	0.2	7.9	7.9	50.0	50.0
84	32.2	0.5	11.8	20.4	36.6	63.4
97	4.5	0.1	1.9	2.6	42.1	57.9
111	11.4	0.1	5.3	6.1	46.9	53.1
120	3.9	0.1	1.7	2.2	44.7	55.3

0.5 mg/l bromine enriched plants

Day	Br21A Total Br (µg/l)	Br21A stdev	Br21A Inorganic Br (µg/l)	Br21A Organic Br (µg/l)	Br21A %Inorganic Br	Br21A %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	720	13.6	720	n.d.	100	n.d.
8	4232	40.3	4232	n.d.	100	n.d.
12	6141	31.1	6141	n.d.	100	n.d.
15	6769	43.4	6769	n.d.	100	n.d.
19	3667	33.2	3667	n.d.	100	n.d.
22	1873	18.6	1873	n.d.	100	n.d.
26	1507	11.1	1507	n.d.	100	n.d.
29	1264	5.3	1263	n.d.	100	n.d.
34	644	2.9	644	n.d.	100	n.d.
40	215	14.0	215	n.d.	100	n.d.
50	231	2.3	20.1	211	8.7	91.3
69	922	3.8	798	125	86.5	13.5
84	396	2.1	301	95.4	75.9	24.1
97	130	1.6	91.9	38.1	70.7	29.3
111	93.5	1.9	51.4	42.1	55.0	45.0
120	68.0	3.7	35.4	32.6	52.0	48.0

Day	Br21B Total Br (µg/l)	Br21B stdev	Br21B Inorganic Br (µg/l)	Br21B Organic Br (µg/l)	Br21B %Inorganic Br	Br21B %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	128	1.4	128	n.d.	100	n.d.
8	1544	7.3	1544	n.d.	100	n.d.
12	2732	19.3	2732	n.d.	100	n.d.
15	1485	27.6	1485	n.d.	100	n.d.
19	1724	40.6	1649	75.5	95.6	4.4
22	1356	3.4	1090	266	80.4	19.6
26	2527	21.5	2527	n.d.	100	n.d.
29	1505	33.2	1505	n.d.	100	n.d.
34	1293	16.8	1293	n.d.	100	n.d.
40	1326	34.1	1326	n.d.	100	n.d.
50	796	4.6	82.8	713.1	10.4	89.6
69	699	10.5	642	56.9	91.9	8.1
84	227	2.7	213	14.5	93.6	6.4
97	197	1.4	197	n.d.	100	n.d.
111	348	2.5	300	48.8	86.0	14.0
120	144	8.0	116	28.1	80.5	19.5

Day	Br22A Total Br (µg/l)	Br22A stdev	Br22A Inorganic Br (µg/l)	Br22A Organic Br (µg/l)	Br22A %Inorganic Br	Br22A %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	347	8.2	347	n.d.	100	n.d.
8	4816	47.6	4816	n.d.	100	n.d.
12	12006	98.6	12006	n.d.	100	n.d.
15	3688	31.2	3688	n.d.	100	n.d.
19	1076	12.7	1076	n.d.	100	n.d.
22	519	12.5	519	n.d.	100	n.d.
26	777	17.7	777	n.d.	100	n.d.
29	590	2.8	590	n.d.	100	n.d.
34	540	7.7	540	n.d.	100	n.d.
40	51.7	0.0	51.7	n.d.	100	n.d.
50	47.3	2.4	4.0	43.3	8.4	91.6
69	130	1.0	98.2	31.6	75.7	24.4
84	183	2.3	159	24.4	86.7	13.3
97	131	0.4	131	n.d.	100	n.d.
111	134	2.0	116	18.0	86.6	13.4
120	55.8	3.3	46.2	9.6	82.8	17.2

Day	Br22B Total Br (µg/l)	Br22B stdev	Br22B Inorganic Br (µg/l)	Br22B Organic Br (µg/l)	Br22B %Inorganic Br	Br22B %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	39.9	0.9	39.9	n.d.	100	n.d.
8	1321	11.3	1321	n.d.	100	n.d.
12	2601	41.2	2601	n.d.	100	n.d.
15	1521	9.5	1521	n.d.	100	n.d.
19	1182	23.0	1182	n.d.	100	n.d.
22	644	21.8	644	n.d.	100	n.d.
26	684	20.2	684	n.d.	100	n.d.
29	604	16.8	604	n.d.	100	n.d.
34	461	3.7	461	n.d.	100	n.d.
40	472	12.1	180	292	38.1	61.9
50	324	1.4	36.1	288	11.1	88.9
69	253	2.0	231	22.8	91.0	9.0
84	147	0.4	123	24.2	83.6	16.4
97	121	2.2	100	20.1	83.3	16.7
111	42.3	0.7	17.1	25.2	40.4	59.6
120	36.2	0.5	8.3	27.9	22.9	77.1

5 mg/l bromine enriched plants

Day	Br31A Total Br (µg/l)	Br31A stdev	Br31A Inorganic Br (µg/l)	Br31A Organic Br (µg/l)	Br31A %Inorganic Br	Br31A %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	6792	38.9	6792	n.d.	100	n.d.
8	56933	29.2	56933	n.d.	100	n.d.
12	71572	297	71573	n.d.	100	n.d.
15	47056	542	47055	n.d.	100	n.d.
19	29813	137	29813	n.d.	100	n.d.
22	17243	190	17243	n.d.	100	n.d.
26	12633	108	12633	n.d.	100	n.d.
29	5084	73.4	5084	n.d.	100	n.d.
34	9022	87.2	9022	n.d.	100	n.d.
40	9531	40.5	9531	n.d.	100	n.d.
50	5280	16.7	500	4779	9.5	90.5
69	2713	21.3	2034	679	75.0	25.0
84	655	10.1	288	367	44.0	56.0
97	320	2.7	159	161	49.8	50.2
111	544	3.3	345	199	63.5	36.6
120	362	14.7	224	138	61.8	38.2

Day	Br31B Total Br (µg/l)	Br31B stdev	Br31B Inorganic Br (µg/l)	Br31B Organic Br (µg/l)	Br31B %Inorganic Br	B31B %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	10781	171	10781	n.d.	100	n.d.
8	55384	20.0	55384	n.d.	100	n.d.
12	36734	332	36734	n.d.	100	n.d.
15	18255	126	18255	n.d.	100	n.d.
19	13930	232	13930	n.d.	100	n.d.
22	7539	50.3	7392	148	98	2
26	7669	105	7669	n.d.	100	n.d.
29	8880	125	8880	n.d.	100	n.d.
34	5221	15.0	5221	n.d.	100	n.d.
40	2562	48.6	2562	n.d.	100	n.d.
50	1464	2.2	120	1344	8.2	91.8
69	740	3.7	301	439	40.7	59.3
84	369	0.2	140	229	37.9	62.1
97	232	6.2	105	127	45.3	54.7
111	338	6.0	162	176	47.9	52.1
120	182	6.3	61.1	120	33.7	66.3

Day	Br32A Total Br (µg/l)	Br32A stdev	Br32A Inorganic Br (µg/l)	Br32A Organic Br (µg/l)	Br32A %Inorganic Br	Br32A %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	7647	31.8	7647	n.d.	100	n.d.
8	57434	81.9	57434	n.d.	100	n.d.
12	46139	482	46139	n.d.	100	n.d.
15	16246	156	16246	n.d.	100	n.d.
19	14946	16.6	14946	n.d.	100	n.d.
22	6593	48.5	6593	n.d.	100	n.d.
26	5849	39.3	5849	n.d.	100	n.d.
29	3182	44.7	3182	n.d.	100	n.d.
34	1799	8.7	1799	n.d.	100	n.d.
40	2733	3.6	2733	n.d.	100	n.d.
50	139	3.5	8.7	130	6.3	93.8
69	90.0	1.4	22.3	67.7	24.8	75.2
84	56.4	1.2	17.1	39.3	30.3	69.7
97	42.3	0.7	12.0	30.3	28.4	71.6
111	122	1.4	82.6	39.1	67.9	32.1
120	91.7	4.3	57.8	33.9	63.0	37.0

Day	Br32B Total Br (µg/l)	Br32B stdev	Br32B Inorganic Br (µg/l)	Br32B Organic Br (µg/l)	Br32B %Inorganic Br	Br32B %Organic Br
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	6151	49.4	6151	n.d.	100	n.d.
8	73543	32.4	73543	n.d.	100	n.d.
12	84680	360	84680	n.d.	100	n.d.
15	30918	236	30918	n.d.	100	n.d.
19	22426	171	22426	n.d.	100	n.d.
22	11008	60.8	11008	n.d.	100	n.d.
26	10884	126	10884	n.d.	100	n.d.
29	6673	84.7	6673	n.d.	100	n.d.
34	5116	33.7	5116	n.d.	100	n.d.
40	2163	21.9	480	1684	22.2	77.8
50	654	3.5	60.6	594	9.3	90.7
69	331	6.6	199	132	60.1	39.9
84	437	3.5	303	134	69.4	30.6
97	2311	3.6	185	45.8	80.2	19.8
111	249	2.9	144	105	57.8	42.2
120	168	0.8	72.2	95.8	43.0	57.0

stdev - Standard Deviation
n.d. – not detected

Table 27. Bromine mass balance.

Fraction	Control	0.05 mg/l	0.5 mg/l	5 mg/l
% Leached	47.7 ± 6.4	15.3 ± 7.9	20.3 ± 3.9	28.6 ± 13.6
% Remain in plant	2.6 ± 2.1	0.55 ± 0.04	0.9 ± 0.8	0.4 ± 0.3
% Volatile	49.6 ± 7.9	84.1 ± 7.9	78.9 ± 4.4	71.1 ± 13.9
Initial iodine amount in plant (µg)	14.8 ± 6.6	441 ± 231	4029 ± 1073	27593 ± 11389

Table 28. Bromine mass balance – extend table.

Control plants

DCBC (μg) - Calculated total Br (dry weight based)

Bcon1A	Bcon1B	Bcon2A	Bcon2B	Average Bcon
23.5	11.5	16.0	8.4	14.8

Total Bromine (μg/l)

Day	Bcon1A	Bcon1B	Bcon2A	Bcon2B	Average Bcon
0	n.d.	n.d.	n.d.	n.d.	n.d.
5	3.7	2.2	2.6	31.9	10.1
8	19.6	6.6	0.2	3.6	7.5
12	201	17.9	24.3	4.6	62.3
15	105	69.5	104	93.1	92.8
19	63.6	54.5	82.5	65.4	66.5
22	n.d.	10.6	n.d.	91.0	25.4
26	n.d.	n.d.	n.d.	9.1	2.3
29	n.d.	3.3	1.9	10.2	3.9
34	n.d.	n.d.	n.d.	4.1	1.0
40	n.d.	n.d.	n.d.	15.2	3.8
50	2.5	2.0	4.7	7.2	4.1
69	2.0	1.1	2.5	5.9	2.9
84	2.2	1.4	1.8	7.4	3.2
97	1.1	0.9	0.6	4.6	1.8
111	1.2	2.0	2.5	2.1	1.9
120	2.4	1.4	2.4	1.0	1.8

Volume (ml)

Day	Bcon1A	Bcon1B	Bcon2A	Bcon2B	Average Bcon
0	30.0	30.0	30.0	30.0	30.0
5	28.0	28.3	27.5	29.0	28.2
8	33.0	30.0	31.5	30.0	31.1
12	34.0	30.0	32.0	31.0	31.8
15	30.5	30.2	30.5	30.5	30.4
19	28.0	29.5	29.5	28.7	28.9
22	28.1	29.0	28.5	28.5	28.5
26	28.0	29.0	29.0	28.5	28.6
29	29.0	29.4	28.5	28.5	28.9
34	28.0	29.0	28.8	28.0	28.5
40	28.3	27.1	28.6	29.1	28.3
50	29.0	29.6	29.3	28.5	29.1
69	20.0	30.0	30.0	30.0	27.5
84	28.7	29.2	29.0	29.0	29.0
97	28.4	27.9	27.8	28.5	28.2
111	28.6	29.1	29.4	29.0	29.0
120	27.8	29.7	28.7	28.5	28.7

Bromine amount in leached solution (μg)

Day	Bcon1A	Bcon1B	Bcon2A	Bcon2B	Average Bcon
0	n.d.	n.d.	n.d.	n.d.	n.d.
5	0.1	0.1	0.1	0.9	0.3
8	0.6	0.2	n.d.	0.1	0.2
12	6.9	0.5	0.8	0.1	2.0
15	3.2	2.1	3.2	2.8	2.8
19	1.8	1.6	2.4	1.9	1.9
22	n.d.	0.3	n.d.	2.6	0.7
26	n.d.	n.d.	n.d.	0.3	0.1
29	n.d.	0.1	0.1	0.3	0.1
34	n.d.	n.d.	n.d.	0.1	n.d.
40	n.d.	n.d.	n.d.	0.4	0.1
50	0.1	0.1	0.1	0.2	0.1
69	n.d.	n.d.	0.1	0.2	0.1
84	0.1	n.d.	0.1	0.2	0.1
97	n.d.	n.d.	n.d.	0.1	0.1
111	n.d.	0.1	0.1	0.1	0.1
120	0.1	n.d.	0.1	n.d.	0.1
sum	12.9	5.2	6.9	10.4	8.7

Bromine amount remain in plant (μg)

Bcon1A	Bcon1B	Bcon2A	Bcon2B	Average Bcon
1.1	n.d.	0.5	n.e.	0.5

Bromine mass balance

Fraction	Bcon1A	Bcon1B	Bcon2A	Bcon2B	Average Bcon
% Leached	55	45	43.3	n.e.	47.7
% Remain in plant	4.5	0.3	3.0	n.e.	2.6
% Volatile	40.5	54.7	53.7	n.e.	49.6
% Total	100	100	100	n.e.	

0.05 mg/l bromine enriched plants

DCBC (µg) - Calculated total Br (dry weight based)

Br11A	Br11B	Br12A	Br12B	Average Br1
762	275	460	269	441

Total Bromine (µg/l)

Day	Br11A	Br11B	Br12A	Br12B	Average Br1
0	n.d.	n.d.	n.d.	n.d.	n.d.
5	12.5	12.6	92.1	81.1	49.6
8	176	307	855	392	432.4
12	353	386	1042	505	571.4
15	82.2	112	395	221	202.5
19	111	71.0	267	139	146.8
22	57.5	12.3	430	87.0	146.7
26	87.7	22.5	185	48.6	85.9
29	146	26.9	42.6	73.6	72.3
34	230	46.3	117.9	27.8	105.4
40	210	41.0	85.1	36.1	93.0
50	201	80.6	56.4	30.5	92.2
69	192	81.6	39.8	15.8	82.2
84	121	40.0	23.7	32.2	54.3
97	64.0	19.7	16.0	4.5	26.1
111	39.5	12.9	7.7	11.4	17.9
120	21.9	8.8	13.5	3.9	12.0

Volume (ml)

Day	Br11A	Br11B	Br12A	Br12B	Average Br1
0	30.0	30.0	30.0	30.0	30.0
5	28.5	28.0	27.0	28.0	27.9
8	29.8	31.2	33.0	31.2	31.3
12	30.5	32.5	31.5	32.3	31.7
15	29.9	30.0	31.0	30.5	30.4
19	29.0	29.0	27.7	30.5	29.1
22	28.5	28.0	27.7	29.0	28.3
26	26.7	28.5	28.7	29.0	28.2
29	28.0	28.3	28.0	28.5	28.2
34	27.5	30.2	3.4	28.4	22.4
40	29.5	28.7	28.5	29.2	29.0
50	29.5	29.5	29.0	29.1	29.3
69	30.0	29.7	29.8	28.8	29.6
84	29.0	28.9	28.1	28.8	28.7
97	28.5	28.5	27.9	29.0	28.5
111	29.0	28.5	28.8	27.9	28.6
120	28.7	28.4	26.7	28.5	28.1

Bromine amount in leached solution (μg)

Day	Br11A	Br11B	Br12A	Br12B	Average Br1
0	n.d.	n.d.	n.d.	n.d.	n.d.
5	0.4	0.4	2.5	2.3	1.4
8	5.2	9.6	28.2	12.2	13.5
12	10.8	12.5	32.8	16.3	18.1
15	2.5	3.3	12.2	6.7	6.1
19	3.2	2.1	7.4	4.2	4.3
22	1.6	0.3	11.9	2.5	4.2
26	2.3	0.6	5.3	1.4	2.4
29	4.1	0.8	1.2	2.1	2.0
34	6.3	1.4	0.4	0.8	2.4
40	6.2	1.2	2.4	1.1	2.7
50	5.9	2.4	1.6	0.9	2.7
69	5.7	2.4	1.2	0.5	2.4
84	3.5	1.2	0.7	0.9	1.6
97	1.8	0.6	0.4	0.1	0.7
111	1.1	0.4	0.2	0.3	0.5
120	0.6	0.2	0.4	0.1	0.3
sum	61.4	39.3	108.9	52.5	65.4

Bromine amount remain in plant (μg)

Br11A	Br11B	Br12A	Br12B	Average Br1
4.1	1.6	2.4	n.e.	2.7

Bromine mass balance

Fraction	Br11A	Br11B	Br12A	Br12B	Average Br1
% Leached	8.1	14.3	23.7	n.e.	15.3
% Remain in plant	0.5	0.6	0.5	n.e.	0.55
% Volatile	91.4	85.1	75.8	n.e.	84.1
% Total	100	100	100	n.e.	

0.5 mg/l bromine enriched plants

DCBC (µg) - Calculated total Br (dry weight based)

Br21A	Br21B	Br22A	Br22B	Average Br2
3646	2684	4869	4917	4029

Total Bromine (µg/l)

Day	Br21A	Br21B	Br22A	Br22B	Average Br2
0	n.d.	n.d.	n.d.	n.d.	n.d.
5	720	128	347	39.9	308.8
8	4232	1544	4816	1321	2978
12	6141	2732	12006	2601	5870
15	6769	1485	3688	1521	3366
19	3667	1724	1076	1182	1912
22	1873	1356	519	644	1098
26	1507	2527	777	684	1373.7
29	1263	1505	590	604	990.6
34	644	1293	540	461	734
40	215	1326	51.7	472	516
50	231	796	47.3	324	350
69	922	699	130	254	501
84	396	227	183	147	239
97	130	197	131	121	145
111	93.5	349	134	42.3	155
120	68.0	143.8	55.8	36.2	75.9

Volume (ml)

Day	Br21A	Br21B	Br22A	Br22B	Average Br2
0	30.0	30.0	30.0	30.0	30.0
5	30.0	28.0	27.0	27.0	28.0
8	32.0	29.5	31.5	28.5	30.4
12	34.0	32.0	34.5	31.5	33.0
15	29.9	31.3	30.0	31.0	30.6
19	28.7	30.5	30.0	29.5	29.7
22	29.5	29.0	29.0	29.0	29.1
26	29.5	29.5	28.4	28.7	29.0
29	29.0	29.5	28.5	29.0	29.0
34	28.9	29.0	28.4	31.5	29.5
40	29.1	28.8	29.1	29.7	29.2
50	27.7	27.8	28.5	29.3	28.3
69	29.5	21.7	29.0	24.7	26.2
84	28.1	26.0	26.7	28.5	27.3
97	28.3	27.9	28.4	29.0	28.4
111	27.8	28.0	28.0	29.0	28.2
120	27.5	29.0	27.5	29.0	28.3

Bromine amount in leached solution (μg)

Day	Br21A	Br21B	Br22A	Br22B	Average Br2
0	n.d.	n.d.	n.d.	n.d.	n.d.
5	21.6	3.6	9.4	1.1	8.6
8	135.4	45.6	151.7	37.6	90.5
12	208.8	87.4	414.2	81.9	193.7
15	202.4	46.5	110.6	47.2	102.8
19	105.2	52.6	32.3	34.9	56.7
22	55.2	39.3	15.1	18.7	32.0
26	44.4	74.5	22.1	19.6	39.9
29	36.6	44.4	16.8	17.5	28.7
34	18.6	37.5	15.3	14.5	21.6
40	6.3	38.2	1.5	14.0	15.1
50	6.4	22.1	1.3	9.5	9.9
69	27.2	15.2	3.8	6.3	13.1
84	11.1	5.9	4.9	4.2	6.5
97	3.7	5.5	3.7	3.5	4.1
111	2.6	9.8	3.8	1.2	4.4
120	1.9	4.2	1.5	1.1	2.1
sum	887.5	532.1	808.0	312.8	629.8

Bromine amount remain in plant (μg)

Br21A	Br21B	Br22A	Br22B	Average Br2
36.7	42.0	2.6	n.e.	27.1

Bromine mass balance

Fraction	Br21A	Br21B	Br22A	Br22B	Average Br2
% Leached	24.3	19.8	16.6	n.e.	20.3
% Remain in plant	1.0	1.6	0.06	n.e.	0.9
% Volatile	74.7	78.6	83.3	n.e.	78.9
% Total	100	100	100	n.e.	

5 mg/l bromine enriched plants

DCBC (µg) - Calculated total Br (dry weight based)

Br31A	Br31B	Br32A	Br32B	Average Br3
35608	11668	27076	36019	27593

Total Bromine (µg/l)

Day	Br31A	Br31B	Br32A	Br32B	Average Br3
0	n.d.	n.d.	n.d.	n.d.	n.d.
5	6792	10781	7647	6151	7843
8	56933	55384	57434	73543	60824
12	71572	36734	46139	84680	59781
15	47055	18255	16246	30918	28119
19	29813	13930	14946	22426	20279
22	17243	7540	6593	11008	10596
26	12633	7669	5849	10884	9259
29	5084	8880	3182	6673	5955
34	9022	5221	1799	5116	5290
40	9531	2562	2733	2163	4247
50	5280	1464	139	654	1884
69	2713	740	89.9	331	969
84	655	369	56.4	437	379
97	320	232	42.3	231	206
111	544	338	122	249	313
120	362	182	91.7	168	201

Volume (ml)

Day	Br31A	Br31B	Br32A	Br32B	Average Br3
0	30.0	30.0	30.0	30.0	30.0
5	30.0	28.5	27.7	29.5	28.9
8	31.0	31.0	32.0	33.0	31.8
12	33.0	30.7	30.0	33.0	31.7
15	32.0	30.5	28.5	30.0	30.3
19	29.5	29.0	27.5	29.0	28.8
22	27.5	28.5	27.3	29.0	28.1
26	29.0	28.5	27.0	28.0	28.1
29	28.0	29.0	27.0	29.0	28.3
34	28.0	28.0	28.5	29.0	28.4
40	26.9	29.5	28.1	27.9	28.1
50	27.0	28.4	28.0	28.5	28.0
69	27.0	28.9	28.5	29.5	28.5
84	27.5	28.5	27.9	27.5	27.9
97	28.3	27.7	27.4	28.1	27.9
111	28.5	28.5	28.5	26.0	27.9
120	27.5	28.5	25.0	27.4	27.1

Bromine amount in leached solution (μg)

Day	Br31A	Br31B	Br32A	Br32B	Average Br3
0	n.d.	n.d.	n.d.	n.d.	n.d.
5	204	307	212	182	227
8	1765	1717	1838	2427	1931
12	2362	1128	1384	2794	1894
15	1506	557	463	928	851
19	880	404	411	650	583
22	474	215	180	319	298
26	366	219	158	305	260
29	142	258	85.9	194	168
34	253	146	51.3	148	150
40	256	75.6	76.8	60.4	119
50	143	41.6	3.9	18.6	52.7
69	73.3	21.4	2.6	9.8	27.6
84	18.0	10.5	1.6	12.0	10.6
97	9.1	6.4	1.2	6.5	5.8
111	15.5	9.6	3.5	6.5	8.7
120	9.9	5.2	2.3	4.6	5.4
sum	8476	5120	4875	8065	6592

Bromine amount remain in plant (μg)

Br31A	Br31B	Br32A	Br32B	Average Br3
96.4	80.9	26.6	n.e.	68.0

Bromine mass balance

Fraction	Br31A	Br31B	Br32A	Br32B	Average Br3
% Leached	23.8	43.9	18.0	n.e.	28.6
% Remain in plant	0.3	0.7	0.1	n.e.	0.3
% Volatile	75.9	55.4	81.9	n.e.	71.1
% Total	100	100	100	n.e.	

n.d. – not detected

n.e. – not examined

Table 29. Bromine enriched plants decomposition - dissolved carbon decomposition data.

Control plants

Day	Bcon1A TC average (mg/l)	Bcon1A TC stdev.	Bcon1A IC Average (mg/l)	Bcon1A IC stdev.	Bcon1A TOC (mg/l)	Bcon1A %TOC	Bcon1A %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	127	1.2	54.8	0.2	72.1	56.8	43.2
8	418	1.1	201	0.3	217	51.9	48.1
12	1637	26.9	379	4.1	1258	76.9	23.1
15	432	2.0	147	125.1	285	65.9	34.1
19	838	0.9	150	3.8	690	82.4	17.6
22	317	0.6	94.2	0.9	223	70.3	29.7
26	207	0.4	59.8	0.8	147	71.1	28.9
29	122	0.4	39.2	0.3	83.2	68.0	32.0
34	150	0.8	25.9	0.01	124	82.7	17.3
40	126	1.0	11.9	0.1	114	90.5	9.5
50	101	0.4	7.4	0.3	94.1	92.7	7.3
69	98.3	1.1	9.9	0.1	88.4	90.0	10.0
84	43.3	1.2	3.5	0	39.9	92.0	8.0
97	48.5	0.2	7.8	0.2	40.6	83.8	16.2
111	33.0	0.5	6.5	0.1	26.4	80.3	19.7
120	40.9	0.2	8.5	0	32.4	79.1	20.9

Day	Bcon1B TC Average (mg/l)	Bcon1B TC stdev.	Bcon1B IC Average (mg/l)	Bcon1B IC stdev.	Bcon1B TOC (mg/l)	Bcon1B %TOC	Bcon1B %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	41.4	0.4	21.9	0.3	19.5	47.1	52.9
8	224	0.9	131	0.1	93.3	41.6	58.4
12	582	9.6	110	1.4	472	81.1	18.9
15	270	1.4	142	1.4	128	47.4	52.6
19	208	2.1	23.8	0.3	184	88.6	11.4
22	87.0	0.1	22.4	0.2	64.6	74.3	25.8
26	59.5	0.6	18.7	0.1	40.7	68.5	31.5
29	43.1	0.4	11.3	0.2	31.8	73.7	26.3
34	51.5	0.1	12.1	0	39.4	76.6	23.5
40	52.9	1.1	11.5	0.1	41.4	78.3	21.7
50	46.8	0.1	9.4	0	37.4	79.9	20.1
69	42.1	0.1	6.1	0.1	36.1	85.7	14.4
84	54.0	0.1	5.3	0.2	48.6	90.1	9.9
97	43.9	0.3	5.4	0.2	38.5	87.7	12.4
111	31.6	0.2	5.6	0.3	25.9	82.1	17.9
120	25.1	0	3.7	0	21.5	85.4	14.6

Day	Bcon2A TC Average (mg/l)	Bcon2A TC stdev.	Bcon2A IC Average (mg/l)	Bcon2A IC stdev.	Bcon2A TOC (mg/l)	Bcon2A %TOC	Bcon2A %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	63.7	0.2	38.1	0.1	25.6	40.2	59.8
8	430	1.6	330	0.7	100	23.3	76.8
12	862	1.8	236	0.1	626	72.7	27.3
15	99.0	0.2	42.4	0.5	56.6	57.2	42.8
19	430	6.8	73.7	0.7	357	82.9	17.1
22	121	0.3	38.1	0.3	83.0	68.5	31.5
26	132	0.6	55.6	0.3	76.7	58.0	42.1
29	98.5	0.0	36.0	0.5	62.5	63.4	36.6
34	119	0.6	41.9	0.3	76.9	64.7	35.3
40	96.0	1.3	36.0	0.1	60.0	62.5	37.5
50	93.5	0.6	29.8	0.3	63.7	68.1	31.9
69	75.9	15.3	15.6	0.6	60.2	79.4	20.6
84	57.2	0.4	13.8	0.2	43.5	76.0	24.0
97	35.7	0.3	6.1	0	29.5	82.8	17.2
111	36.5	0.2	9.6	0.1	26.9	73.6	26.4
120	34.3	0.3	9.0	0	25.3	73.8	26.2

Day	Bcon2B TC Average (mg/l)	Bcon2B TC stdev.	Bcon2B IC Average (mg/l)	Bcon2B IC stdev.	Bcon2B TOC (mg/l)	Bcon2B %TOC	Bcon2B %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	47.5	0.5	26.1	0.2	21.4	45.1	55.0
8	290	1.3	192.9	1.2	97.0	33.5	66.5
12	700	0.7	162.0	1.2	538	76.9	23.1
15	160	0.9	79.2	0.1	80.8	50.5	49.5
19	248	0.7	43.2	0.3	205	82.6	17.4
22	99.7	0.4	29.3	0.5	70.4	70.6	29.4
26	61.2	0.3	26.9	0.2	34.3	56.0	44.0
29	64.8	0.2	24.4	0.5	40.4	62.3	37.7
34	124	0.4	38.4	0.1	85.8	69.1	30.9
40	94.2	0.4	27.5	0.1	66.7	70.8	29.2
50	59.7	0.1	18.7	0.3	41.0	68.7	31.3
69	104	0.3	19.2	0.2	84.9	81.5	18.5
84	129	0.4	19.2	0.2	110.0	85.2	14.8
97	119	0.2	20.1	0.2	98.4	83.0	17.0
111	71.6	0.3	13.1	0.1	58.5	81.7	18.3
120	75.5	0.1	11.1	0.2	64.4	85.3	14.7

0.05 mg/l bromine enriched plants

Day	Br11A TC Average (mg/l)	Br11A TC stdev.	Br11A IC Average (mg/l)	Br11A IC stdev.	Br11A TOC (mg/l)	Br11A %TOC	Br11A %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	61.1	0.2	31.7	0.1	29.4	48.1	51.9
8	306	0.9	187	0.8	119	39.0	61.1
12	1101	4.2	295	2.2	806	73.2	26.8
15	1047	2.1	247	0.5	801	76.4	23.6
19	994	3.8	196	0.6	798	80.3	19.7
22	276	1.0	120	0.0	156	56.4	43.6
26	240	0.9	93.0	0.4	147	61.3	38.7
29	156	0.6	50.5	1.0	105	67.6	32.4
34	209	2.1	67.9	0.4	141	67.6	32.5
40	99.8	0.5	26.6	0.2	73.3	73.4	26.6
50	122	0.4	20.6	0.5	102	83.2	16.8
69	120	0.4	7.3	0.1	112	93.9	6.1
84	71.7	0.2	n.d.	n.d.	71.7	100	n.d.
97	43.6	0.4	n.d.	n.d.	43.6	100	n.d.
111	32.2	0.1	n.d.	n.d.	32.2	100	n.d.
120	27.6	0.1	n.d.	n.d.	27.6	100	n.d.

Day	Br11B TC Average (mg/l)	Br11B TC stdev.	Br11B IC Average (mg/l)	Br11B IC stdev.	Br11B TOC (mg/l)	Br11B %TOC	Br11B %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	68.3	0.3	29.2	0.1	39.1	57.3	42.7
8	306	0.9	154	3.7	152	49.7	50.4
12	754	1.1	144	2.8	610	80.9	19.1
15	237	2.2	112	0.5	125	52.8	47.2
19	331	1.2	53.9	1.2	277	83.7	16.3
22	84.2	0.3	27.8	0.4	56.4	67.0	33.0
26	86.2	0.1	27.7	0.2	58.5	67.9	32.1
29	56.6	0.1	17.0	0.1	39.7	70.0	30.0
34	80.7	0.1	20.4	0.2	60.4	74.8	25.2
40	69.4	0.0	14.3	0.1	55.1	79.4	20.6
50	45.2	0.3	1.9	0.1	43.4	95.9	4.1
69	42.2	0.3	n.d.	n.d.	42.2	100	n.d.
84	20.6	0.1	n.d.	n.d.	20.6	100	n.d.
97	16.5	0.1	n.d.	n.d.	16.5	100	n.d.
111	13.6	0.1	n.d.	n.d.	13.6	100	n.d.
120	13.7	0.2	n.d.	n.d.	13.7	100	n.d.

Day	Br12A TC Average (mg/l)	Br12A TC stdev.	Br12A IC Average (mg/l)	Br12A IC stdev.	Br12A TOC (mg/l)	Br12A %TOC	Br12A %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	103	0.4	30.4	0	72.2	70.3	29.7
8	536	8.1	219	1.3	317	59.2	40.8
12	139	1.0	29.7	0.07	109	78.6	21.4
15	374	2.2	188	0.1	185	49.6	50.4
19	652	6.2	119	0.6	533	81.8	18.2
22	170	0.3	58.5	0.3	112	65.6	34.4
26	138	0.6	48.7	0	89.0	64.6	35.4
29	163	1.0	57.5	0.5	105	64.6	35.4
34	101	0.8	32.0	0.6	68.7	68.2	31.8
40	85.4	0.7	19.5	0.1	65.9	77.2	22.9
50	84.0	0.6	13.4	0.1	70.6	84.0	16.0
69	78.1	8.7	9.1	0	69.0	88.3	11.7
84	48.0	0.5	6.3	0.1	41.7	87.0	13.0
97	45.9	0.4	6.9	0	39.0	85.0	15.0
111	31.7	0.3	7.2	0	24.5	77.2	22.8
120	45.5	0.5	9.1	0.1	36.4	80.1	19.9

Day	Br12B TC Average (mg/l)	Br12B TC stdev.	Br12B IC Average (mg/l)	Br12B IC stdev.	Br12B TOC (mg/l)	Br12B %TOC	Br12B %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	92.0	0.5	45.9	0.3	46.1	50.1	49.9
8	405	0.9	213.3	0.7	192	47.4	52.6
12	934	1.7	181.1	0.2	753	80.6	19.4
15	197	1.8	87.5	0.4	111	55.9	44.1
19	342	1.4	61.0	0.2	281	82.2	17.8
22	104	0.4	35.6	0.2	68.2	65.7	34.3
26	78.5	0.6	36.1	0.1	42.4	54.0	46.0
29	50.0	0.1	15.2	0.2	34.8	69.7	30.4
34	45.9	0.1	13.8	0.1	32.2	70.0	30.0
40	63.1	0.6	14.9	0.2	48.1	76.3	23.7
50	63.9	0.1	16.4	0	47.5	74.4	25.7
69	49.8	0.5	13.3	0.2	36.5	73.2	26.8
84	75.5	0.0	16.4	0.1	59.1	78.3	21.8
97	22.8	0.1	6.1	0.2	16.7	73.3	26.8
111	33.9	0.0	6.3	0.2	27.6	81.4	18.6
120	20.5	0.2	3.6	0.1	16.9	82.6	17.4

0.5 mg/l bromine enriched plants

Day	Br21A TC Average (mg/l)	Br21A TC stdev.	Br21A IC Average (mg/l)	Br21A IC stdev.	Br21A TOC (mg/l)	Br21A %TOC	B21A %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	137	0.2	73.8	0.3	63.5	46.2	53.8
8	390	1.7	237	1.2	152	39.1	60.9
12	1518	3.5	376	2.3	1142	75.2	24.8
15	1211	2.1	311	0.6	900	74.4	25.7
19	1134	2.1	248	0.8	886	78.1	21.9
22	320	1.6	140	0.4	180	56.2	43.8
26	277	1.7	109	1.3	168	60.7	39.3
29	87.9	1.2	32.3	0.2	55.6	63.3	36.7
34	177	0.4	64.3	1.4	112	63.6	36.4
40	144	0.6	45.0	0.2	99.3	68.8	31.2
50	113	0.4	25.6	0	87.0	77.3	22.7
69	94.0	0.4	19.2	1.8	74.8	79.6	20.4
84	60.8	0.1	12.0	0.1	48.8	80.3	19.7
97	44.6	2.5	9.7	0.4	35.0	78.3	21.7
111	41.1	0.1	8.1	2.4	33.1	80.3	19.7
120	38.5	0.3	11.0	0	27.5	71.5	28.5

Day	Br21B TC Average (mg/l)	Br21B TC stdev.	Br21B IC Average (mg/l)	Br21B IC stdev.	Br21B TOC (mg/l)	Br21B %TOC	Br21B %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	36.4	0.4	19.5	0.4	16.9	46.5	53.6
8	268	16.5	161	0.3	107	39.9	60.1
12	1096	10.6	336	0.6	760	69.4	30.7
15	301	2.4	212	1.1	89.5	29.7	70.3
19	739	5.7	149	1.3	590	79.8	20.2
22	258	0.4	79.6	0.6	179	69.2	30.8
26	303	0.1	75.6	0.1	227	75.0	25.0
29	117	0.0	31.5	0.2	85.0	73.0	27.0
34	138	0.6	40.6	0.4	97.2	70.5	29.5
40	132	0.6	42.0	0.2	89.7	68.1	31.9
50	128	0.9	44.4	0	84.2	65.5	34.5
69	118	0.1	38.7	0.5	79.7	67.3	32.7
84	45.4	0.2	17.2	0.1	28.2	62.0	38.0
97	57.6	0.5	14.6	0.1	43.0	74.7	25.3
111	76.4	0.4	16.4	0.0	60.0	78.5	21.5
120	50.9	0.3	12.4	0.1	38.5	75.6	24.5

Day	Br22A TC Average (mg/l)	Br22A TC stdev.	Br22A IC Average (mg/l)	Br22A IC stdev.	Br22A TOC (mg/l)	Br22A %TOC	Br22A %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	41.1	0.3	12.2	0.1	28.9	70.3	29.7
8	277	0.3	122	0.7	156	56.1	44.0
12	1208	5.7	289	0.8	919	76.1	23.9
15	320	3.3	165	1.4	155	48.4	51.6
19	374	0.6	64.6	0.2	310	82.7	17.3
22	82.3	0.4	24.6	0.3	57.8	70.2	29.8
26	72.9	0.2	23.8	0.7	49.1	67.4	32.6
29	39.6	0.6	10.8	0.3	28.8	72.7	27.3
34	46.7	0.6	11.9	0.5	34.8	74.5	25.5
40	35.4	0.4	4.3	0.2	31.1	88.0	12.0
50	54.6	0.4	5.6	0.1	49.0	89.7	10.3
69	41.9	0.5	4.6	0.1	37.2	88.9	11.1
84	26.3	0.4	2.2	0.3	24.1	91.5	8.5
97	22.8	0.1	3.4	0	19.4	85.0	15.0
111	22.8	0.1	4.2	0.1	18.6	81.6	18.4
120	20.3	0.2	4.3	0.1	16.0	78.9	21.1

Day	Br22B TC Average (mg/l)	Br22B TC stdev.	Br22B IC Average (mg/l)	Br22B IC stdev.	Br22B TOC (mg/l)	Br22B %TOC	Br22B %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	9.2	0	5.8	0.1	3.4	36.8	63.2
8	155	0.7	83.8	0.5	71.6	46.1	53.9
12	754	5.7	194	1.8	560	74.3	25.7
15	214	1.4	91.5	42.8	123	57.3	42.7
19	431	5.5	66.5	0.7	364	84.6	15.4
22	109	0.1	28.4	0.2	80.9	74.0	26.0
26	92.1	0.2	25.4	0.5	66.7	72.4	27.6
29	51.1	0.1	12.0	0.4	39.1	76.5	23.5
34	50.6	0.3	15.1	0.2	35.5	70.2	29.8
40	82.4	0.7	18.4	0.1	64.1	77.7	22.3
50	55.3	0.7	10.8	0.5	44.6	80.6	19.4
69	58.4	4.1	11.6	0.5	46.8	80.1	19.9
84	36.1	0.2	6.5	0.1	29.6	82.1	17.9
97	42.9	0.3	6.4	0.1	36.5	85.0	15.0
111	23.3	0	4.6	0.1	18.7	80.2	19.8
120	26.1	0	3.7	0.1	22.4	85.8	14.2

5 mg/l bromine enriched plants

Day	Br31A TC Average (mg/l)	Br31A TC stdev.	Br31A IC Average (mg/l)	Br31A IC stdev.	Br31A TOC (mg/l)	Br31A %TOC	Br31A %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	65.1	0.4	40.4	0.3	24.7	38.0	62.0
8	507	1.7	275	0.5	232	45.8	54.2
12	1555	4.2	365	2.3	1190	76.5	23.5
15	441	1.4	193	0.4	244	56.2	43.9
19	858	2.1	115	4.2	744	86.7	13.4
22	229	2.0	70.0	0.8	159	69.4	30.6
26	213	1.3	80.8	0.3	132	62.0	38.0
29	137	0.4	39.0	0.3	98.1	71.5	28.5
34	148	1.3	42.5	0.2	105	71.3	28.8
40	166	1.1	55.9	0.5	110	66.2	33.8
50	150	0.4	52.2	0.5	97.7	65.2	34.8
69	130	2.4	37.4	0.2	92.3	71.2	28.8
84	89.9	0.6	16.4	0.2	73.5	81.7	18.3
97	63.8	0.3	10.8	0.1	53.1	83.1	16.9
111	49.3	0.3	7.1	0.1	42.2	85.5	14.5
120	43.2	0.2	6.9	0.1	36.4	84.1	15.9

Day	Br31B TC Average (mg/l)	Br31B TC stdev.	Br31B IC Average (mg/l)	Br31B IC stdev.	Br31B TOC (mg/l)	Br31B %TOC	Br31B %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	123	2.3	70.8	0.1	52.5	42.6	57.4
8	535	2.0	259	0.4	277	51.7	48.3
12	992	1.4	183	0.5	809	81.6	18.4
15	243	2.4	102	0.03	140	57.8	42.2
19	448	0.6	59.3	0.2	389	86.8	13.3
22	120	0.6	26.7	0.7	92.8	77.7	22.3
26	115	0.3	42.3	0.6	72.2	63.1	37.0
29	81.2	1.3	25.7	0.4	55.5	68.3	31.7
34	109	0.6	30.0	0.6	79.0	72.5	27.5
40	150	0.9	57.1	0.3	92.9	62.0	38.0
50	88.0	0.3	18.5	0.1	69.5	79.0	21.0
69	73.9	0.1	12.0	0.04	61.9	83.8	16.2
84	43.5	0.1	5.9	0.1	37.6	86.5	13.5
97	32.0	0.2	4.3	0.02	27.7	86.5	13.5
111	32.2	0.2	4.1	0.1	28.1	87.2	12.8
120	25.3	0.1	4.0	0.02	21.3	84.3	15.7

Day	Br32A TC Average (mg/l)	Br32A TC stdev.	Br32A IC Average (mg/l)	Br32A IC stdev.	Br32A TOC (mg/l)	Br32A %TOC	Br32A %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	88.1	0.2	27.8	0.1	60.3	68.4	31.6
8	562	0.0	207	1.3	355	63.1	36.9
12	1123	5.0	173	0.2	950	84.6	15.4
15	283	1.3	99.0	0.1	184	65.0	35.0
19	485	3.5	58.4	0.7	426	88.0	12.0
22	126	0.2	30.3	0.4	96.0	76.0	24.0
26	160	1.1	32.9	0.5	128	79.5	20.5
29	103	0.1	17.6	0	85.3	82.9	17.1
34	81.0	0.8	11.3	0	69.7	86.0	14.0
40	110	0.7	20.8	0.4	88.8	81.0	19.0
50	63.7	0.8	8.0	0.2	55.7	87.5	12.5
69	56.0	0.1	5.0	0.2	51.0	91.1	8.9
84	50.3	0.4	2.5	0.1	47.8	95.0	5.0
97	51.8	0.4	3.1	0.02	48.7	94.0	6.0
111	38.3	0.2	3.1	0.1	35.2	91.8	8.2
120	47.5	0.4	4.1	0.04	43.4	91.4	8.6

Day	Br32B TC Average (mg/l)	Br32B TC stdev.	Br32B IC Average (mg/l)	Br32B IC stdev.	Br32B TOC (mg/l)	Br32B %TOC	Br32B %IC
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	70.1	0.5	38.2	0.1	31.9	45.5	54.5
8	731	2.0	366	3.1	364	49.9	50.1
12	1726	12.7	433	2.7	1293	74.9	25.1
15	371	0.6	208	1.4	163	43.9	56.1
19	591	4.3	114	0.5	476	80.7	19.4
22	180	0.3	71.1	0.8	108	60.4	39.6
26	170	1.0	51.8	0.3	118	69.5	30.5
29	120	0.7	25.6	0.2	94.1	78.6	21.4
34	115	0.6	25.5	0.5	89.8	77.9	22.2
40	74.0	0.3	20.5	0.2	53.5	72.3	27.7
50	86.5	0.6	14.5	0.1	72.0	83.3	16.7
69	57.0	0.2	6.7	0.1	50.3	88.3	11.7
84	55.6	0.2	4.7	0.1	50.9	91.5	8.5
97	44.9	0.2	3.8	0.1	41.1	91.6	8.4
111	41.4	0.1	2.8	0.1	38.5	93.2	6.9
120	49.2	0.3	3.7	0.04	45.4	92.4	7.6

TC - Total carbon

IC – Inorganic carbon

TOC – Total organic carbon

stdev - Standard deviation

n.d. – not detected

Table 30. Bromine enriched plants decomposition - NO_3 decomposition data.

Control plants

Day	Bcon1A (mg/l)	Bcon1B (mg/l)	Bcon2A (mg/l)	Bcon2B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	227	85.8	109	118
8	386	258	256	224
12	288	207	177	191
15	232	91.9	213	115
19	147	n.d.	113	n.d
22	71.9	55.2	43.5	42.2
26	31.8	n.d.	21.7	15.4
29	22.3	28.4	14.0	22.1
34	13.4	23.0	8.9	36.1
40	0.3	26.9	5.1	47.2
50	0.4	9.1	3.6	35.0
69	0.3	0.6	1.1	73.5
84	7.6	0.2	0.4	65.9
97	0.2	0.1	0.6	n.d.
111	n.d.	n.d.	0.8	23.4
120	0.2	0.1	n.d.	26.3

0.05 mg/l bromine enriched plants

Day	Br11A (mg/l)	Br11B (mg/l)	Br12A (mg/l)	Br12B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	87.5	165	193	172
8	367	332	449	334
12	281	308	313	312
15	276	206	207	191
19	262	56.8	79.4	79.7
22	138	27.0	29.5	186
26	n.d	13.8	19.5	10.2
29	56.1	6.4	17.6	4.7
34	25.8	2.7	17.8	1.7
40	12.8	1.3	16.6	3.2
50	10.6	5.6	5.2	0.8
69	24.7	64.1	1.2	0.7
84	83.3	65.6	0.4	0.8
97	n.d.	n.d.	0.2	0.6
111	46.2	26.3	n.d.	1.3
120	34.2	21.3	0.4	0.7

0. 5 mg/l bromine enriched plants

Day	Br21A (mg/l)	Br21B (mg/l)	Br22A (mg/l)	Br22B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	209	68.5	163	7.7
8	383	255	400	149
12	356	277	343	161
15	530	258	149	112
19	172	265	21.8	120
22	100	37.0	1.7	84.7
26	62.2	245	n.d.	n.d.
29	25.7	109	0.7	51.8
34	11.0	71.0	0.7	36.3
40	0.2	n.d.	0.7	33.6
50	1.0	18.9	0.5	29.8
69	1.6	31.6	0.2	27.1
84	0.3	16.6	0.3	16.1
97	0.4	n.d.	0.2	n.d.
111	0.4	20.7	0.3	9.2
120	n.d.	n.d.	n.d.	n.d.

5 mg/l bromine enriched plants

Day	Br31A(mg/l)	Br31B(mg/l)	Br32A(mg/l)	Br32B(mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	119	200	211	138
8	383	336	494	413
12	368	165	330	325
15	375	51.5	193	163
19	252	14.4	104	78.5
22	119	0.9	53.2	36.4
26	58.0	0.6	41.0	26.6
29	27.4	0.2	31.8	14.4
34	14.4	0.1	19.7	6.2
40	10.2	n.d.	0.4	2.1
50	3.5	n.d.	0.2	1.4
69	3.2	0.6	0.1	0.4
84	1.6	0.2	0.7	n.d.
97	0.6	0.2	0.5	0.1
111	0.3	n.d.	0.8	0.1
120	n.d.	n.d.	n.d.	n.d.

n.d. – not detected

Table 31. Bromine enriched plants decomposition - NO_2 decomposition data.

Control plants

Day	Bcon1A (mg/l)	Bcon1B (mg/l)	Bcon2A (mg/l)	Bcon2B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	3.6	3.7	3.8	n.d.
8	92.6	17.3	63.8	23.8
12	n.d.	27.8	45.6	19.2
15	n.d.	10.2	44.3	22.2
19	12.7	3.1	23.5	15.0
22	0.6	2.6	9.8	23.7
26	0.1	1.2	4.8	12.2
29	0.1	0.9	2.2	25.1
34	n.d.	0.4	1.1	32.7
40	n.d.	0.2	0.2	20.9
50	0.1	n.d.	n.d.	6.5
69	n.d.	0.1	n.d.	7.1
84	2.2	0.3	0.4	3.7
97	0.3	n.d.	0.2	1.2
111	n.d.	n.d.	n.d.	0.3
120	0.1	0.1	0.1	0.1

0. 05 mg/l bromine enriched plants

Day	Br11A (mg/l)	Br11B (mg/l)	Br12A (mg/l)	Br12B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	4.8	n.d.	3.3	6.2
8	4.6	10.2	109.4	45.0
12	12.6	45.5	n.d.	129
15	12.0	25.1	159	88.5
19	11.7	2.2	64.9	33.3
22	4.6	0.4	32.8	161
26	4.3	n.d.	17.7	1.4
29	3.8	0.1	12.6	0.7
34	3.3	0.2	7.6	0.2
40	25.5	1.1	1.8	0.3
50	51.4	41.3	n.d.	0.3
69	106	43.7	n.d.	0.1
84	5.1	0.3	0.1	0.4
97	3.4	1.0	n.d.	n.d.
111	3.2	0.3	n.d.	0.1
120	n.d.	n.d.	n.d.	n.d.

0. 5 mg/l bromine enriched plants

Day	Br21A (mg/l)	Br21B (mg/l)	Br22A (mg/l)	Br22B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	31.7	2.7	0.2	n.d.
8	185	14.4	11.6	2.2
12	315	42.0	112	4.3
15	250	46.1	21.2	9.5
19	192	118	0.9	23.1
22	61.3	10.1	0.1	12.5
26	17.7	220	0.1	8.4
29	4.4	118	0.2	9.2
34	0.8	94.5	0.1	5.9
40	0.1	7.4	0.1	3.5
50	0.1	20.5	0.2	2.6
69	n.d.	8.3	0.1	1.4
84	n.d.	1.3	0.1	n.d.
97	n.d.	0.6	n.d.	n.d.
111	n.d.	0.5	n.d.	n.d.
120	n.d.	0.1	n.d.	n.d.

5 mg/l bromine enriched plants

Day	Br31A (mg/l)	Br31B (mg/l)	Br32A (mg/l)	Br32B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	1.8	2.6	5.9	0.2
8	0.9	6.0	113	5.0
12	n.d.	7.2	119	0.3
15	1.4	3.4	101	n.d.
19	0.8	0.4	41.2	0.5
22	0.7	0.1	15.4	n.d.
26	n.d.	0.1	7.1	n.d.
29	0.2	n.d.	2.4	0.2
34	0.2	0.1	0.3	n.d.
40	0.1	0.3	n.d.	n.d.
50	0.1	0.1	0.1	0.1
69	0.1	0.1	0.1	n.d.
84	n.d.	0.1	n.d.	0.2
97	n.d.	n.d.	n.d.	0.1
111	0.1	n.d.	0.1	n.d.
120	n.d.	n.d.	n.d.	0.3

Table 32. Bromine enriched plants decomposition - SO_4 decomposition data.

Control plants

Day	Bcon1A (mg/l)	Bcon1B (mg/l)	Bcon2A (mg/l)	Bcon2B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	8.9	4.3	4.9	3.0
8	23.6	14.0	21.6	10.9
12	48.7	19.4	28.6	20.9
15	38.4	7.5	36.8	12.7
19	18.6	4.4	20.6	6.4
22	19.9	8.1	15.1	11.1
26	6.4	5.2	12.4	5.4
29	4.1	5.1	13.3	8.1
34	6.3	3.8	11.2	14.6
40	2.6	5.3	9.0	12.0
50	1.0	2.3	9.2	4.7
69	4.6	1.1	5.7	10.6
84	3.5	0.3	3.7	9.5
97	1.7	0.5	4.8	4.8
111	1.8	0.6	2.0	3.1
120	1.8	0.8	1.8	4.2

0. 05 mg/l bromine enriched plants

Day	Br11A (mg/l)	Br11B (mg/l)	Br12A (mg/l)	Br12B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	3.4	13.4	6.9	10.9
8	27.4	24.5	29.0	30.9
12	48.1	39.7	47.9	53.2
15	38.5	23.4	30.8	27.2
19	30.4	6.1	17.5	15.1
22	29.2	8.1	13.0	28.3
26	25.0	7.2	10.2	7.4
29	21.2	6.6	7.8	8.4
34	20.1	6.5	7.6	3.8
40	16.2	4.2	7.1	5.4
50	12.1	3.0	4.7	4.3
69	12.1	4.5	2.3	2.9
84	5.8	2.6	1.7	6.7
97	2.8	1.7	1.1	0.8
111	3.2	1.6	0.9	2.2
120	2.1	1.3	2.3	0.7

0. 5 mg/l bromine enriched plants

Day	Br21A (mg/l)	Br21B (mg/l)	Br22A (mg/l)	Br22B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	8.4	0.9	1.8	0.3
8	28.4	11.8	16.1	7.5
12	62.0	31.9	51.7	21.4
15	55.9	23.3	26.1	16.7
19	43.2	28.1	8.4	14.6
22	33.4	14.7	5.9	8.6
26	25.5	37.3	6.0	6.3
29	15.2	19.8	5.1	5.5
34	14.0	16.2	5.2	4.1
40	1.6	6.6	3.3	3.7
50	3.6	10.4	1.6	3.0
69	5.7	11.5	0.1	2.7
84	2.8	3.2	0.1	2.0
97	1.3	3.3	0.4	2.0
111	1.4	5.4	0.7	1.5
120	1.4	3.7	0.7	2.1

5 mg/l bromine enriched plants

Day	Br31A (mg/l)	Br31B (mg/l)	Br32A (mg/l)	Br32B (mg/l)
1	n.d.	n.d.	n.d.	n.d.
5	5.2	11.4	4.0	6.4
8	39.3	38.5	30.8	56.0
12	62.5	36.0	47.1	72.3
15	51.8	23.7	25.2	34.2
19	37.7	18.0	19.6	23.1
22	26.2	13.9	11.5	18.4
26	16.0	10.5	11.9	16.6
29	16.1	10.4	9.5	13.7
34	15.7	12.3	5.0	11.5
40	17.1	7.4	0.5	9.3
50	17.1	7.1	n.d.	5.5
69	0.1	5.2	0.1	3.6
84	9.8	1.6	0.1	2.4
97	2.2	0.3	0.1	1.1
111	1.9	0.2	0.9	1.1
120	1.9	0.2	n.d.	1.6

n.d. – not detected

Table 33. Iodine enriched plants decomposition - iodine release data.

Control plants

Day	Icon1A Total I (µg/l)	Icon1A stdev	Icon1A Inorganic I (µg/l)	Icon1A Organic I (µg/l)	Icon1A %Inorganic I	Icon1A %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	0.60	0.05	0.01	0.59	1.67	98.3
9	1.02	0.03	0.42	0.59	41.6	58.4
12	0.34	0.07	n.d.	0.34	n.d.	100
15	1.24	0.14	n.d.	1.24	n.d.	100
19	0.80	0.02	0.33	0.47	41.5	58.5
23	0.72	0.03	0.35	0.37	49	52
26	1.95	0.78	0.08	1.87	4	96
29	0.74	0.05	0.05	0.69	6.9	93.1
33	0.70	0.62	0.09	0.61	12.6	87.4
40	0.64	0.03	0.08	0.56	11.8	88.2
47	0.88	0.01	0.06	0.82	7.1	92.9
54	2.41	0.27	0.08	2.33	3.4	96.6
61	2.07	0.02	0.12	1.95	5.65	94.35
75	0.82	0.05	0.20	0.63	23.8	76.2

Day	Icon1B Total I (µg/l)	Icon1B stdev	Icon1B Inorganic I (µg/l)	Icon1B Organic I (µg/l)	Icon1B %Inorganic I	Icon1B %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	0.61	0.08	0.09	0.52	14.7	85.3
9	2.11	0.01	1.37	0.74	65	35
12	2.10	0.05	0.39	1.72	18.4	81.6
15	1.95	0.02	0.28	1.68	14.1	85.9
19	1.54	0.03	0.86	0.67	56.1	43.9
23	0.71	0.04	0.32	0.39	45.1	54.9
26	1.56	0.07	0.10	1.46	6.4	93.6
29	0.58	0.02	0.25	0.34	42.5	57.5
33	1.17	0.05	0.17	0.99	14.8	85.2
40	0.46	0.02	0.16	0.30	35.2	64.8
47	0.91	0.01	0.19	0.72	20.9	79.1
54	0.83	0.02	0.19	0.64	22.9	77.1
61	0.81	0.03	0.05	0.76	6.6	93.4
75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Day	Icon2A Total I (µg/l)	Icon2A stdev	Icon2A Inorganic I (µg/l)	Icon2A Organic I (µg/l)	Icon2A %Inorganic I	Icon2A %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	0.86	0.02	0.04	0.81	5	95
9	2.22	0.03	1.44	0.78	65	35
12	1.03	0.04	0.01	1.03	0.5	99.5
15	0.65	0.03	n.d.	0.65	n.d.	100
19	0.65	0.02	0.24	0.41	36.5	63.5
23	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
26	0.87	0.03	0.07	0.80	7.8	92.2
29	0.33	0.03	0.11	0.22	32.9	67.1
33	0.11	0.03	0.07	0.04	60.6	39.4
40	0.37	0.01	0.14	0.23	37.8	62.2
47	0.33	0.00	0.05	0.28	16.2	83.8
54	0.57	0.01	0.04	0.53	7.7	92.3
61	0.70	0.02	0.08	0.61	12	88
75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

0.05 mg/l iodine enriched plants

Day	I11A Total I (µg/l)	I11A stdev	I11A Inorganic I (µg/l)	I11A Organic I (µg/l)	I11A %Inorganic I	I11A %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	82.5	0.9	18.0	64.5	21.8	78.2
9	153	1.2	137	16.0	89.5	10.5
12	103	0.2	18.3	84.2	17.9	82.1
15	37.7	0.4	n.d.	37.7	n.d.	100
19	32.6	0.2	22.6	10.0	69.3	30.7
23	25.3	0.1	11.9	13.5	46.8	53.2
26	16.3	0.1	1.8	14.6	10.7	89.3
29	16.3	0.2	7.1	9.2	43.7	56.3
33	9.7	0.2	4.0	5.6	41.6	58.4
40	14.9	0.2	4.8	10.1	32.1	68.0
47	11.9	0.1	3.6	8.3	30.0	70.0
54	13.2	0.2	4.3	8.9	32.7	67.3
61	9.0	0.2	2.7	6.3	30.0	70.0
75	15.8	0.1	2.6	13.2	16.6	83.4

Day	I11B Total I (µg/l)	I11B stdev	I11B Inorganic I (µg/l)	I11B Organic I (µg/l)	I11B %Inorganic I	I11B %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	106	1.1	23.3	82.3	22.0	78.0
9	266	3.6	231	35.4	86.7	13.3
12	165	1.2	29.2	135.7	17.7	82.3
15	65.9	0.3	9.2	56.7	14.0	86.0
19	45.7	0.5	31.5	14.2	68.9	31.1
23	30.4	0.2	13.6	16.9	44.5	55.5
26	30.9	0.5	0.1	30.8	0.2	99.8
29	22.5	0.0	12.5	10.1	55.3	44.7
33	16.9	0.0	7.9	9.0	46.5	53.5
40	16.8	0.4	7.7	9.1	45.7	54.3
47	25.3	0.4	10.5	14.8	41.5	58.5
54	29.5	0.3	10.7	18.9	36.1	63.9
61	11.4	0.2	3.4	8.0	29.8	70.2
75	8.2	0.1	2.6	5.6	31.7	68.3

Day	I12A Total I (µg/l)	I12A stdev	I12A Inorganic I (µg/l)	I12A Organic I (µg/l)	I12A %Inorganic I	I12A %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	14.2	0.0	3.0	11.2	21.2	78.8
9	43.5	0.5	41.1	2.4	94.5	5.5
12	67.7	0.9	13.2	54.5	19.4	80.6
15	49.3	0.6	6.8	42.5	13.7	86.3
19	26.1	0.2	16.0	10.1	61.4	38.7
23	23.5	0.2	8.2	15.3	n.d.	n.d.
26	31.9	0.1	4.7	27.2	14.6	85.4
29	15.8	0.1	6.4	9.4	40.7	59.3
33	18.8	0.4	5.8	13.0	31.0	69.0
40	26.1	0.7	8.5	17.6	32.4	67.6
47	21.1	0.2	6.6	14.5	31.2	68.8
54	16.1	0.1	4.9	11.2	30.5	69.5
61	14.7	0.3	4.1	10.6	28.1	71.9
75	13.9	0.2	3.1	10.8	22.3	77.7

0.5 mg/l iodine enriched plants

Day	I21A Total I (µg/l)	I21A stdev	I21A Inorganic I (µg/l)	I21A Organic I (µg/l)	I21A %Inorganic I	I21A %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	1357	8.0	302	1055	22.2	77.8
9	1588	19.9	1430	158	90.0	10.0
12	725	4.2	153	572	21.2	78.9
15	365	2.3	71.1	294	19.5	80.5
19	239	1.1	193	46.2	80.7	19.3
23	79.7	1.1	12.3	67.4	15.4	84.6
26	154	3.0	26.7	127	17.4	82.6
29	74.7	0.3	50.4	24.3	67.4	32.6
33	26.1	0.7	22.4	3.7	86.0	14.1
40	67.2	0.5	30.7	36.5	45.6	54.4
47	45.2	1.0	17.6	27.6	39.0	61.0
54	54.1	0.1	22.6	31.5	41.7	58.3
61	38.9	0.1	13.9	25.0	35.8	64.2
75	37.6	0.1	3.1	34.4	8.3	91.7

Day	I21B Total I (µg/l)	I221B stdev	I221B Inorganic I (µg/l)	I221B Organic I (µg/l)	I221B %Inorganic I	I221B %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	664	3.1	141	523	21.2	78.8
9	1036	2.0	922	115	88.9	11.1
12	500	4.1	117	384	23.3	76.7
15	387	5.4	88.3	299	22.8	77.2
19	209	2.8	11.1	198	5.3	94.7
23	76.6	1.7	11.4	65.3	14.8	85.2
26	129	0.5	22.2	107	17.2	82.8
29	42.4	0.5	27.7	14.7	65.4	34.6
33	96.2	1.4	71.0	25.3	73.8	26.2
40	12.1	0.1	6.0	6.1	49.9	50.1
47	85.0	0.6	47.3	37.7	55.7	44.3
54	31.9	1.0	15.3	16.6	48.1	51.9
61	30.1	0.2	9.1	21.0	30.2	69.8
75	34.9	0.2	2.6	32.3	7.4	92.6

Day	I22A Total I (µg/l)	I22A stdev	I22A Inorganic I (µg/l)	I22A Organic I (µg/l)	I22A %Inorganic I	I22A %Organic I
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	582	2.1	136	447	23.3	76.7
9	1929	14.5	1833	95.7	95.0	5.0
12	1045	16.0	231	814	22.1	77.9
15	619	9.2	128	491	20.6	79.4
19	424	5.7	349	74.5	82.4	17.6
23	94.9	2.1	16.0	78.9	16.9	83.1
26	168	0.8	28.6	139	17.1	82.9
29	136	2.3	76.2	59.3	56.3	43.8
33	39.9	1.5	37.9	2.0	95.0	5.0
40	41.4	0.3	23.9	17.5	57.8	42.2
47	27.0	0.2	12.8	14.1	47.6	52.4
54	16.1	0.5	5.9	10.2	36.6	63.4
61	15.7	0.3	4.1	11.6	26.2	73.8
75	37.9	0.5	2.7	35.2	7.1	92.9

stdev - Standard Deviation

n.d. – not detected

Table 34. Iodine mass balance – extend table.

Control plants

DCIC (µg) - Calculated total I (dry weight based)

Icon1A	Icon1B	Icon2A	Average	
1.55	0.99	2.24	1.59	0.63

Total Iodine (µg/l)

Day	Icon1A	Icon1B	Icon2A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	0.6	0.6	0.9	0.7	0.1
9	1.0	2.1	2.2	1.8	0.7
12	0.3	2.1	1.0	1.2	0.9
15	1.2	2.0	0.6	1.3	0.7
19	0.8	1.5	0.6	1.0	0.5
23	0.7	0.7	n.d.	0.5	0.4
26	2.0	1.6	0.9	1.5	0.5
29	0.7	0.6	0.3	0.5	0.2
33	0.7	1.2	0.1	0.7	0.5
40	0.6	0.5	0.4	0.5	0.1
47	0.9	0.9	0.3	0.7	0.3
54	2.4	0.8	0.6	1.3	1.0
61	2.1	0.8	0.7	1.2	0.8
75	0.8	n.d.	n.d.	0.3	0.5

Volume (ml)

Day	Icon1A	Icon1B	Icon2A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	26.1	29.0	29.4	28.2	1.8
9	29.8	31.0	25.4	28.7	2.9
12	30.7	29.9	32.3	31.0	1.2
15	29.4	28.4	29.7	29.2	0.7
19	29.7	29.5	30.8	30.0	0.7
23	30.1	29.9	30.0	30.0	0.1
26	29.1	29.1	29.5	29.2	0.2
29	29.5	29.3	29.4	29.4	0.1
33	29.4	29.4	29.0	29.3	0.2
40	29.8	28.3	27.5	28.5	1.2
47	29.7	29.0	29.0	29.2	0.4
54	28.8	28.3	28.4	28.5	0.3
61	28.7	28.8	29.2	28.9	0.3
75	29.0	28.4	28.5	28.6	0.3

Iodine amount in leached solution (μg)

Day	Icon1A	Icon1B	Icon2A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	0.02	0.02	0.03	0.02	0.01
9	0.03	0.07	0.06	0.05	0.02
12	0.01	0.06	0.03	0.04	0.03
15	0.04	0.06	0.02	0.04	0.02
19	0.02	0.05	0.02	0.03	0.01
23	0.02	0.02	n.d.	0.01	0.01
26	0.06	0.05	0.03	0.04	0.02
29	0.02	0.02	0.01	0.02	0.01
33	0.02	0.03	0.00	0.02	0.02
40	0.02	0.01	0.01	0.01	0.00
47	0.03	0.03	0.01	0.02	0.01
54	0.07	0.02	0.02	0.04	0.03
61	0.06	0.02	0.02	0.03	0.02
75	0.02	0.00	n.d.	0.01	0.01

Iodine amount remain in plant (μg)

	Icon1A	Icon1B	Icon2A	Average	stdev
	0.34	0.24	0.28	0.29	0.05

Iodine mass balance

Fraction	Icon1A	Icon1B	Icon2A	Average	stdev
% leached	28.1	45.5	11.1	28.3	17.2
%remain in plant	21.8	24.6	12.3	19.6	6.45
% volatile	50.1	29.9	76.6	52.2	23.4
%total	100	100	100		

0.05 mg/l Iodine enriched plants

DCIC (µg) - Calculated total I (dry weight based)

I11A	I11B	I12A	Average	stdev
20.2	30.3	15.2	21.9	7.73

Total Iodine (µg/l)

Day	I11A	I11B	I12A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	82.5	106	14.2	67.4	47.5
9	153	266	43.4	154	111
12	103	165	67.7	112	49.3
15	37.7	65.9	49.3	50.9	14.2
19	32.6	45.7	26.1	34.8	10.0
23	25.3	30.4	23.5	26.4	3.6
26	16.3	30.8	31.9	26.4	8.7
29	16.3	22.5	15.8	18.2	3.7
33	9.7	16.9	18.8	15.1	4.8
40	14.9	16.8	26.1	19.2	6.0
47	11.9	25.3	21.1	19.4	6.8
54	13.2	29.5	16.1	19.6	8.7
61	9.0	11.4	14.7	11.7	2.9
75	15.8	8.2	13.9	12.7	4.0

Volume (ml)

Day	I11A	I11B	I12A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	27.2	27.0	27.2	27.1	0.1
9	32.0	33.6	29.1	31.6	2.3
12	10.5	11.0	10.3	10.6	0.4
15	29.0	29.3	30.3	29.5	0.7
19	26.0	29.3	29.3	28.2	1.9
23	29.1	29.5	29.4	29.3	0.2
26	30.0	28.4	29.4	29.3	0.8
29	29.6	29.3	28.4	29.1	0.6
33	28.6	28.4	29.1	28.7	0.4
40	28.6	29.6	28.7	29.0	0.6
47	28.4	29.0	29.2	28.9	0.4
54	29.1	28.4	28.6	28.7	0.4
61	29.9	29.8	29.2	29.6	0.4
75	30.1	28.4	29.4	29.3	0.9

Iodine amount in leached solution (µg)

Day	I11A	I11B	I12A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	2.24	2.85	0.39	1.83	1.28
9	4.88	8.94	1.26	5.03	3.84
12	1.08	1.81	0.70	1.20	0.57
15	1.09	1.93	1.49	1.50	0.42
19	0.85	1.34	0.76	0.98	0.31
23	0.74	0.90	0.69	0.78	0.11
26	0.49	0.88	0.94	0.77	0.24
29	0.48	0.66	0.45	0.53	0.11
33	0.28	0.48	0.55	0.43	0.14
40	0.43	0.50	0.75	0.56	0.17
47	0.34	0.73	0.62	0.56	0.20
54	0.38	0.84	0.46	0.56	0.24
61	0.27	0.34	0.43	0.35	0.08
75	0.48	0.23	0.41	0.37	0.13
	14.03	22.42	9.90	15.45	7.85

Iodine amount remain in plant (μg)

Day	I11A	I11B	I12A	Average	stdev
	3.66	6.83	3.97	4.82	1.75

Iodine mass balance

Fraction	I11A	I11B	I12A	Average	stdev
% leached	69.4	73.9	65.3	69.5	4.3
%remain in plant	18.2	22.5	26.2	22.3	4.06
% volatile	12.4	3.6	8.5	8.2	4.4
%total	100	100	100		

0.5 mg/l Iodine enriched plants

DCIC (µg) - Calculated total I (dry weight based)

I21A	I21B	I22A	Average	stdev
194	82.6	155	143.6	56.3

Total Iodine (µg/l)

Day	I21A	I21B	I22A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	1357	664	582	868	426
9	1588	1036	1929	1518	451
12	725	500	1045	758	274
15	365	387	619	457	141
19	239	209	424	291	116
23	79.7	76.6	94.9	83.7	9.8
26	154	129	168	150	19.6
29	74.7	42.4	135.5	84.2	47.3
33	26.1	96.2	39.9	54.1	37.1
40	67.2	12.1	41.4	40.2	27.6
47	45.2	85.0	27.0	52.4	29.7
54	54.1	31.9	16.1	34.0	19.1
61	38.9	30.1	15.7	28.2	11.7
75	37.5	34.9	37.9	36.8	1.6

Volume (ml)

Day	I21A	I21B	I22A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	27.6	27.5	27.5	27.5	0.1
9	36.0	31.8	36.6	34.8	2.6
12	30.6	30.1	29.7	30.1	0.5
15	29.6	28.1	30.4	29.4	1.2
19	29.6	29.6	28.8	29.3	0.5
23	29.4	29.4	29.4	29.4	0.0
26	29.4	28.5	28.6	28.8	0.5
29	29.8	28.7	29.3	29.3	0.6
33	28.4	28.7	29.6	28.9	0.6
40	29.2	29.0	29.0	29.1	0.1
47	28.9	29.1	29.4	29.1	0.3
54	28.6	28.3	28.7	28.5	0.2
61	28.4	29.5	29.2	29.0	0.6
75	28.7	29.6	29.2	29.2	0.5

Iodine amount in leached solution (µg)

Day	I21A	I21B	I22A	Average	stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.
5	37.5	18.3	16	23.9	11.8
9	57.2	33.0	70.6	53.6	19.1
12	22.2	15.1	31.0	22.76	8.00
15	10.8	10.9	18.8	13.5	4.61
19	7.09	6.19	12.21	8.49	3.25
23	2.34	2.25	2.79	2.46	0.29
26	4.52	3.67	4.79	4.33	0.58
29	2.23	1.22	3.97	2.47	1.39
33	0.74	2.76	1.18	1.56	1.06
40	1.96	0.35	1.20	1.17	0.81
47	1.31	2.47	0.79	1.52	0.86
54	1.55	0.90	0.46	0.97	0.55
61	1.10	0.89	0.46	0.82	0.33
75	1.08	1.03	1.11	1.07	0.04

Iodine amount remain in plant (µg)

Day	I21A	I21B	I22A	Average	Stdev
	26.7	23.5	25.7	25.3	1.61

Iodine mass balance

Fraction	I21A	I21B	I22A
% leached	78.2	120	107
%remain in plant	13.8	28.5	16.5
% volatile	8	n.a.	n.a.
%total	100	n.a	n.a

stdev - Standard deviation

n.a – not available

n.d. – not detected

Table 35. Atlantic beech (*Fagus Sylvatica*) – bromine decomposition data.

Day	RW1 Average	RW1 stdev	RW2 Average	RW2 stdev	RW3 Average	RW3 stdev	RW4 Average	RW4 stdev
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4	1.03	0.04	1.06	0.02	1.05	0.05	0.91	0.04
7	0.65	0.04	0.65	0.04	2.31	0.03	0.43	0.04
11	0.87	0.03	0.76	0.05	1.36	0.02	0.73	0.01
14	0.79	0.04	0.77	0.10	1.33	0.06	0.91	0.04
18	0.62	0.03	1.62	0.02	0.96	0.03	1.04	0.02
25	0.68	0.02	0.98	0.03	1.83	0.03	1.25	0.01
32	1.14	0.01	1.57	0.08	3.44	0.10	1.56	0.05
39	2.07	0.00	1.66	0.04	3.23	0.03	1.76	0.03
46	1.11	0.03	2.17	0.05	4.32	0.08	1.23	0.02
53	2.02	0.03	1.60	0.04	4.03	0.08	1.22	0.05
66	3.67	0.05	1.59	0.04	4.75	0.06	1.97	0.04
92	6.24	0.09	1.93	0.04	3.20	0.05	2.01	0.05

stdev - Standard deviation

n.d. – not detected

Table 36. Atlantic beech (*Fagus Sylvatica*) – bromine mass balance.

DCBC (µg) - Calculated total Br (dry weight based)

RW1	RW2	RW3	RW4
3.18	2.95	3.99	n.e.

Total Bromine (µg/l)

Day	RW1	RW2	RW3	RW4
1	n.d.	n.d.	n.d.	n.d.
4	1.03	1.06	1.05	0.91
7	0.65	0.65	2.31	0.43
11	0.87	0.76	1.36	0.73
14	0.79	0.77	1.33	0.91
18	0.62	1.62	0.96	1.04
25	0.68	0.98	1.83	1.25
32	1.14	1.57	3.44	1.56
39	2.07	1.66	3.23	1.76
46	1.11	2.17	4.32	1.23
53	2.02	1.60	4.03	1.22
66	3.67	1.59	4.75	1.97
92	6.24	1.93	3.20	2.01

Volume (ml)

Day	RW1	RW2	RW3	RW4
1	30.0	30.0	30.0	30.0
4	28.5	27.2	25.5	27.9
7	28.3	26.6	26.8	27.9
11	28.5	28.9	26.7	29.1
14	29.9	29.2	28.5	29.3
18	28.0	29.0	29.8	29.7
25	30.3	28.5	27.5	28.7
32	28.9	29.1	29.2	29.0
39	27.6	28.5	25.9	29.1
46	28.0	28.7	27.6	29.7
53	28.5	29.1	29.8	29.4
66	28.4	28.5	29.8	28.5
92	26.9	29.8	28.9	29.6

Bromine amount in leached solution (μg)

Day	RW1	RW2	RW3	RW4
1	n.d.	n.d.	n.d.	n.d.
4	0.03	0.03	0.03	0.03
7	0.02	0.02	0.06	0.01
11	0.02	0.02	0.04	0.02
14	0.02	0.02	0.04	0.03
18	0.02	0.05	0.03	0.03
25	0.02	0.03	0.05	0.04
32	0.03	0.05	0.10	0.05
39	0.06	0.05	0.08	0.05
46	0.03	0.06	0.12	0.04
53	0.06	0.05	0.12	0.04
66	0.10	0.05	0.14	0.06
92	0.17	0.06	0.09	0.06
sum	0.59	0.48	0.91	0.44

Bromine amount remain in plant (μg)

RW1	RW2	RW3	RW4
2.4	2.0	2.5	n.e.

Mass balance calculation

Fraction	RW1	RW2	RW3	RW4
% Leached	18.4	15.9	22.5	n.e.
% Remain in plant	75.5	66.1	62.9	n.e.
% Volatile	6.1	18	14.6	n.e.
% Total	100	100	100	n.e.

n.d. – not detected

n.e. – not examined

Table 37. Concentration of iodine, bromine and carbon in soil and soil solution at Sandstone site.

Sandstone core	Depth (cm)	I conc. in soil (mg/kg)	I conc. in soil solution (µg/l)	Br conc. in soil (mg/kg)	Br conc. in soil solution (µg/l)	Total Carbon in soil (%)	DOC conc. in soil solution (mg/l)
1	4-5	3.6	5.8	3.5	15.5	5.4	73.1
	5-7	1.7	4.9	4.0	12.6	3.8	49.4
	7-10	10.0	6.9	2.6	13.4	2.0	31.8
	10-15	9.6	17.3	5.5	21.3	1.4	21.0
	15-20	11.6	16.5	6.0	16.6	1.0	16.0
	20-25	8.0	16.6	6.5	16.3	1.3	15.5
	25-30	4.2	6.8	5.7	7.0	1.2	7.5
	30-35	12.6	2.6	4.2	3.9	0.8	6.8
	35-40	7.9	1.5	4.9	3.1	1.2	5.9
	40-45	10.7	1.0	4.6	2.4	0.8	5.7
	45-50	13.7	4.7	7.0	5.6	1.1	6.0
	50-55	11.4	4.5	4.8	3.7	0.7	5.6
2	4-5	6.8	5.0	4.6	10.1	3.2	70.4
	5-7	4.2	8.6	2.8	15.0	2.4	33.4
	7-10	3.6	12.9	5.4	18.3	2.0	27.3
	10-15	3.5	14.0	6.1	20.4	1.7	21.5
	15-20	9.0	13.8	9.2	17.9	1.6	13.0
	20-25	14.5	6.0	7.8	10.6	1.4	10.7
	25-30	9.4	3.3	7.8	5.9	1.1	7.5
	30-35	8.6	2.2	7.4	4.7	1.0	9.6
	35-40	10.8	1.1	4.1	2.8	0.4	5.4
	40-45	9.9	0.6	4.4	1.4	0.5	5.4
	45-50	8.7	2.3	4.4	3.2	0.5	4.2
	50-55	9.2	0.8	3.9	2.2	0.4	9.6

DOC- Dissolved organic carbon

Table 38. Concentration of iodine, bromine and carbon in soil and soil solution at Carbonate site.

Carbonate core	Depth (cm)	I conc. in soil (mg/kg)	I conc. in soil solution (µg/l)	Br conc. in soil (mg/kg)	Br conc. in soil solution (µg/l)	Total Carbon in soil (%)	DOC conc. in soil solution (mg/l)
1	5-6	7.9	3	7.7	10.8	12.8	33.1
	6-8	9.3	4.4	7.9	14.4	4.7	36.4
	8-10	2.9	5.3	8.6	30	4.9	29
	10-15	11.4	8.2	6.2	30	2.3	24.8
	15-20	9	8.3	7.8	29.8	4.1	14.1
	20-25	9.1	7.1	6.8	20.9	1.8	11.8
	25-30	4.3	9.7	5.4	21.5	1.4	11.7
	30-35	9.2	6.7	6.1	30.9	1.5	9.7
	35-40	10	7.3	7	42.6	1.4	9.7
	40-45	5.2	5.4	5.4	36.7	1.8	8.7
	45-50	6.9	5.2	6.3	29.9	1.9	9.1
	50-55	9.7	7.4	5.9	35.6	2.2	11.9
2	5-6	6.4	3	7.1	11	8.9	23.3
	6-8	5.9	2.9	5.9	11	8.8	26.1
	8-10	6.1	9.7	5.6	26.9	4.2	31.9
	10-15	5.9	9.6	6.2	29.8	2.8	27.1
	15-20	7.8	11.4	5.3	30.2	1.8	20.5
	20-25	3.7	14.8	4.5	25.3	1.3	25.2
	25-30	5.8	15	2.7	25.1	0.8	24.2
	30-35	13.4	5.9	4.3	16.8	0.8	10.5
	35-40	8.8	4.7	7.5	32.9	1.4	9.2
	40-45	3.1	4.4	8.2	32.4	1.7	11.5
	45-50	0.7	4.1	6.4	34.2	1.9	8.1
	50-55	4.7	4.6	7	30.9	2.5	14.1

DOC- Dissolved organic carbon

Table 39. Iodine, bromine speciation in soil solution at Sandstone site.

Sandstone core	Depth (cm)	I conc. in soil solution (µg/l)	% Organic I in soil solution	Br conc. in soil solution (µg/l)	% Organic Br in soil solution
1	4-5	5.8	89.1	15.5	90.1
	5-7	4.9	89.1	12.6	92.7
	7-10	6.9	97.1	13.4	96.4
	10-15	17.3	97.2	21.3	96.8
	15-20	16.5	98.4	16.6	97.9
	20-25	16.6	97.3	16.3	97.6
	25-30	6.8	91	7.0	92.6
	30-35	2.6	95.4	3.9	92.2
	35-40	1.5	84.5	3.1	77.1
	40-45	1.0	91.5	2.4	68.6
	45-50	4.7	91.1	5.6	92.8
	50-55	4.5	88.9	3.7	90.1
2	4-5	5.0	88.8	10.1	87.8
	5-7	8.6	91.9	15.0	91.8
	7-10	12.9	94.9	18.3	94.3
	10-15	14.0	96.1	20.4	95.3
	15-20	13.8	96.1	17.9	95.7
	20-25	6.0	88.4	10.6	87.9
	25-30	3.3	70.9	5.9	83.4
	30-35	2.2	72.9	4.7	93.6
	35-40	1.1	82.6	2.8	87.8
	40-45	0.6	82	1.4	52.8
	45-50	2.3	75.9	3.2	85.2
	50-55	0.8	76.2	2.2	70

Table 40. Iodine, bromine speciation in soil solution at Carbonate site.

Carbonate core	Depth (cm)	I conc. in soil solution (µg/l)	% Organic I in soil solution	Br conc. in soil solution (µg/l)	% Organic Br in soil solution
1	5-6	3.0	100	10.8	77.7
	6-8	4.4	100	14.4	71.2
	8-10	5.3	100	30	59.9
	10-15	8.2	100	30	74.2
	15-20	8.3	99.2	29.8	78.1
	20-25	7.1	95.1	20.9	88.6
	25-30	9.7	95.2	21.5	68.7
	30-35	6.7	90.9	30.9	46.3
	35-40	7.3	89.6	42.6	47.5
	40-45	5.4	89.3	36.7	33.7
	45-50	5.2	88.9	29.9	31.8
	50-55	7.4	96.3	35.6	58.3
2	5-6	3.0	100	11	65.5
	6-8	2.9	100	11	62.4
	8-10	9.7	100	26.9	76.5
	10-15	9.7	99.4	29.8	73.1
	15-20	11.4	99.2	30.2	82.2
	20-25	14.8	99.3	25.3	96.1
	25-30	15	98.5	25.1	83.1
	30-35	5.9	88.8	16.8	59.3
	35-40	4.7	95.2	32.9	59.6
	40-45	4.4	95.5	32.4	66.3
	45-50	4.1	92.8	34.2	52.5
	50-55	4.6	97.6	30.9	69.8

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Erklärung gem. § 8 (3) b) und c) der Promotionsordnung der Naturwissenschaftlich-Mathematischen Gesamtfakultät der Ruprecht-Karls-Universität Heidelberg

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