

## Emissions of volatile halogenated compounds from a meadow in a coastal area of the Baltic Sea

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Chlorine radicals are well-known catalysts in the ozone depletion reactions. This study was undertaken to monitor emissions of chloromethane (CH<sub>3</sub>Cl), an important source of chlorine to the troposphere and stratosphere, from a boreal coastal meadow on the shoreline of brackish-water sea. We sampled volatile organic compounds in the atmosphere above two halophytic vegetation types on three days in July 2007, overall 22 measurements were conducted. Two experimental sites were dominated by *Salicornia europaea* and two sites were covered by mixed vegetation. A variety of substances of anthropogenic and natural origin were identified, the biogenic organic compounds predominating. The vegetation types did not differ markedly in their CH<sub>3</sub>Cl flux rates, the daily flux from *S. europaea* being 10.97 μg m<sup>-2</sup> d<sup>-1</sup> and that from the mixed vegetation 9.92 μg m<sup>-2</sup> d<sup>-1</sup>. The recorded fluxes agree well with those reported from other coastal ecosystems. Emissions from boreal coastal areas might therefore be a relevant CH<sub>3</sub>Cl source on the local and global scales.

### Introduction

Biogenic volatile organic compounds (BVOCs) are atmospheric trace gases released from biogenic sources (e.g. algae, bacteria and higher plants). BVOCs comprise compounds of varying chemical composition from simple saturated and unsaturated hydrocarbons to organic acids and esters. Therefore, these compounds are often divided into subgroups such as nonmethane hydrocarbons (NMHCs) and oxygenated volatile organic compounds (OVOCs) according to their chemical structure and reactivity. Isoprene and monoterpenes followed by alcohols and carbo-

nyl-group containing compounds are the quantitatively predominant compounds or compound groups (Kesselmeier and Staudt 1999). BVOCs usually have atmospheric lifetimes of a few minutes to hours (Kesselmeier and Staudt 1999) and hence participate mainly in the tropospheric processes influencing ozone concentration and the formation of secondary particles.

Since the end of the last decade, halogenated volatile organic compounds (HVOCs) and especially halomethanes (chloro-, bromo-, and iodomethane) have gained increasing attention. In this group of BVOCs, CH<sub>3</sub>Cl and CH<sub>3</sub>Br have relatively long atmospheric lifetimes (1.0

and 0.7 years, respectively, WMO 2007), which enable them to be transported into the stratosphere where they and their degradation products participate significantly in ozone depletion reactions. The global budgets for these compounds were severely imbalanced, with the known sinks outweighing the known sources (WMO 2007), until the discovery of large terrestrial plant sources (Rhew *et al.* 2000, Yokouchi *et al.* 2000, 2002) brought these estimations more into balance. Today, tropical and subtropical vegetation seems to be the major source for chloromethane (Saito and Yokouchi 2006, Yokouchi *et al.* 2007) due to the large coverage of tropical rainforests and their high primary production. Next to the tropics, substantial fluxes have been recorded from coastal wetlands (Rhew *et al.* 2000, 2002, Dimmer *et al.* 2001, Cox *et al.* 2004, Manley *et al.* 2007) and various dryland ecosystems (Rhew *et al.* 2001, Rhew and Abel 2007, Teh *et al.* 2008). According to these studies the extent of the net flux depends strongly on the plant species, the ambient temperature and the amount of photosynthetically active radiation.

Soils are one of the largest known sinks for halomethanes (WMO 2007) and soil reactions have an influence on the net emission flux of HVOCs. On the other hand, the soil and its inhabitants may function as a source for halomethanes. Keppler *et al.* (2000) suggested the abiotic halomethane formation in soils to be a potential source, and the degradation of dead plant material has been shown to produce large amounts of halomethanes under laboratory conditions (Hamilton *et al.* 2003). Moreover, microorganisms living in soils participate in halomethane cycling. Some fungi produce halomethanes (Watling and Harper 1998, Redeker *et al.* 2004) and many bacteria are known to degrade them (McDonald *et al.* 2002, Schäfer *et al.* 2007). The current information indicates that the terrestrial halomethane budget is extremely complex, with multiple formation and degradation processes going on simultaneously in soil.

Being a net result of opposing formation and degradation reactions, the picture of halomethane emissions from terrestrial ecosystems is complex. Therefore, more experimental and monitoring data from different kinds of soil ecosystems are needed. The estimates being extrapolated to

global scale so far are based on measurements representing relatively narrow geographical areas and ecosystem types (Table 1). The variables controlling the emissions from land sources still need to be clarified, as they vary considerably between different locations. In this study, we provide information on chloromethane emissions from a boreal ecosystem on the shoreline of the brackish Baltic Sea. Our main objective was to estimate the chloromethane flux from this ecosystem. The characteristics of the soil samples collected under two vegetation types were determined to obtain information on the abiotic and edaphic parameters most probably affecting hydromorphological features and chloromethane production in boreal coastal areas.

## Material and methods

### Location

Samples were collected from a coastal meadow located on the island Jungfruskär (60°08'23.94"N, 21°04'39.80"E) in the Finnish archipelago national park in the Baltic Sea (salinity in this part of the Baltic Sea 6‰–7.5‰) (Fig. 1). The islands in the archipelago are rocky and the covering soil layer is mostly less than 1-meter thick. These characteristics are a result of the retreating ice mass that peeled off the loose soil material and exposed the bedrock at the end of the last ice age (10 000 B.P.). The sampling location is biogeographically situated in the northernmost part of the temperate to boreal transition zone, also called the hemiboreal zone (Ahti *et al.* 1968). In this region, the duration of the growing season is approximately 180 days per year (Nordseth 1987).

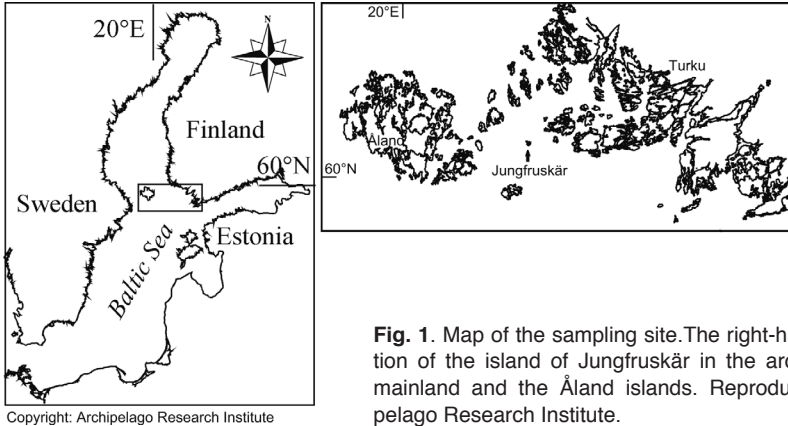
The meadow is located on the eastern side of the island and it surrounds a lagoon-like small bay, and has an area of approximately 1 ha. For our investigations, we chose four sampling sites representing two different kinds of vegetation. In type 1 vegetation, *Salicornia europaea* was almost the only higher plant species present. Type 2 vegetation was a mixture of different plant species and consisted mostly of *Glaux maritima*, *Juncus gerardii*, *Agrostis stolonifera* and *Carex nigra*. Type 2 vegetation covered

**Table 1.** Reported terrestrial net CH<sub>3</sub>Cl emission rates. Fluxes were calculated per hour by dividing the data from the original source given as daily or yearly average fluxes by 24 or 24 × 365 if they were not already given in the units used. The fluxes given in molar units were also transformed into mass unit fluxes.

CH <sub>3</sub> Cl flux area (ng <sup>-1</sup> m <sup>-2</sup> h <sup>-1</sup> )	CH <sub>3</sub> Cl flux dry biomass (ng g <sup>-1</sup> h <sup>-1</sup> )	Location	Predominant vegetation	Reference
924 ± 122	0.74 ± 0.05	NE Colorado U.S. 40°N, 104°W, short grass steppe	<i>Atriplex canescens</i>	Teh <i>et al.</i> (2008)
72–88 × 10 <sup>3</sup>	1367–1494	California U.S. 38°N, 121°W, grassland	<i>Frankenia salina</i> , <i>Cressa truxillensis</i> <i>Lepidium latifolium</i>	Rhew and Abel (2007)
5 × 10 <sup>3</sup>	23	Iriomote Island, Japan 24°N, 123°E, subtropical forest	33 different subtropical and tropical species	Yokouchi <i>et al.</i> (2007) <sup>a</sup>
24 × 10 <sup>3</sup>	140	California U.S. 33°N, 117°W, coastal salt marsh	<i>Spartina foliosa</i> <i>Salicornia virginica</i> <i>Frankenia grandifolia</i> <i>Batis maritima</i>	Manley <i>et al.</i> (2007) <sup>a</sup>
1370	7.99	Glasshouse	<i>Cyatheaceae podophylla</i> <i>Cyatheaceae lepifera</i>	Saito and Yokouchi (2006) <sup>a</sup>
1370	1.83	Tasmania 41°S, 145°E, coastal wetland	<i>Pachyornis arbuscula</i>	Cox <i>et al.</i> (2004)
297 × 10 <sup>3</sup>	582	Ireland 53°N, 9°W coastal marsh	<i>Ranunculus flammula</i> , <i>Apium inundatum</i>	Dimmer <i>et al.</i> (2001)
160 × 10 <sup>3</sup>	297	conifer forest floor (median) peatland (median)	<i>Pinus sylve</i> , <i>Picea sitchensis</i> , <i>Abies alba</i> grasses, mosses	
—	2400 ± 600	California U.S. 32–33°N, 116–117°W, three shrubland biomes	<i>Brassica juncea</i> <i>Carbobrotus edulis</i> <i>Artemisia californica</i>	Rhew <i>et al.</i> (2001) <sup>b</sup>
—	490 ± 170	California U.S. 32°N, 117°W, coastal salt marsh	<i>Larrea tridentata</i> <i>Batis maritima</i> / <i>Salicornia bigelovii</i> <i>Salicornia bigelovii</i>	Rhew <i>et al.</i> (2000)
300	—	New Hampshire U.S. 43°N, 71°W, wetland	<i>Batis maritima</i> <i>Sphagnum</i> spp., <i>Carex</i> spp., shrubs (poor fen) <i>Sphagnum</i> spp. (rich fen)	Varner <i>et al.</i> (1999)
380	—			
3850	—			
605	—			
2314	—			
1178	—			
3702	—			
168	—			
158 × 10 <sup>3</sup>	—			
274 × 10 <sup>3</sup>	—			
1010 × 10 <sup>3</sup>	—			
1103	—			
386	—			

<sup>a</sup> emissions only from vegetation, soil emissions deducted.

<sup>b</sup> daily maximum values.



**Fig. 1.** Map of the sampling site. The right-hand-side panel shows the location of the island of Jungfruskär in the archipelago between the Finnish mainland and the Åland islands. Reproduced with permission of Archipelago Research Institute.

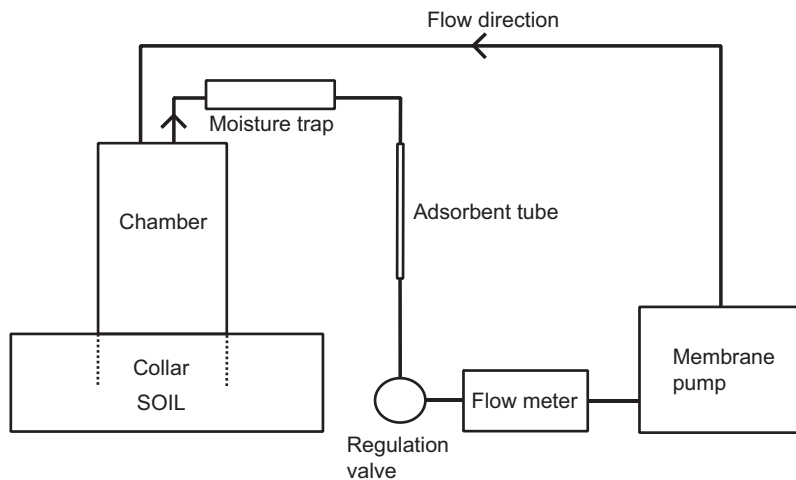
about 70%–80% of the meadow area, while *S. europaea* grew mostly in a few smaller patches where the vegetation was burned off or in areas that were totally or partly flooded by brackish sea water. Below, sampling sites are denoted as *S. europaea* 1 and 2 (vegetation type 1), and mixed vegetation 1 and 2 (vegetation type 2). Other species growing in the meadow were: *Phragmites australis*, *Eleocharis palustris*, *Odontites littoralis* and *Carex panicea*. During the sampling campaign, 10–12 July 2007, the sea water level was unusually high and parts of the meadow vegetation were flooded.

## Gas collection

Gas fluxes were recorded using a dynamic closed chamber method. Our chambers consisted of a transparent acryl glass cylinder (diameter 14.4 cm, wall thickness 0.3 cm, height 20 or 30 cm) with a lid of the same material mounted on an aluminium-plastic base. The base was constructed from an aluminium tube (diameter 11.0 cm) which was surrounded by a plastic ring. The junction was made gastight with silicon gum. The plastic ring had a 2–3-cm-wide channel in which the acryl glass cylinder was placed. When the cylinder was in place, the channel was filled with saturated sodium chloride solution to assure a gas-tight seal. Acryl glass was chosen for the chamber material as it has almost the same inertness and density as mineral glass but is lighter and less fragile. It also shows smaller absorbance of sunlight by letting through UV wavelengths

which do not penetrate mineral glass. Hence the light conditions during the enclosure were kept as natural as possible. Emission cycles (24-hour) were measured for the two vegetation types. The emissions were recorded at five and six different timepoints for *S. europaea* sites and mixed sites, respectively, and on five occasions during the day for control (no vegetation) enclosures. We tried to perform the vegetation and control incubations as evenly spaced as possible throughout days and nights. In every sampling timepoint parallel samples were taken i.e. two plots of the same vegetation type were sampled simultaneously.

The aluminium base was inserted into the soil to a depth of 2–5 cm, and the cylinder was placed on the base channel and sealed as described above. The emission samples were collected on a mixed adsorbent bed (*see below*) by pumping the air from the chamber through the adsorbent tube continuously for two hours. The pump was turned on immediately after the placement of the chamber on its base. The sampling flow was kept at 50–60 ml min<sup>-1</sup> during the pumping. When the collection time was completed, the adsorbent tube was closed with 1/4" Swagelok® fittings with Teflon® ferrules and stored in a cool box until analysis in the laboratory. After the completion of the sampling time the chamber was removed from the base allowing the air surrounding the plant to mix with the ambient air. After the sampling period was completed for a given site, the plant material inside the enclosure was harvested for the determination of the biomass.



**Fig. 2.** A schematic presentation of the used closed chamber system

Five to six samples in 24 hours resulting in total of 22 samples might seem a small dataset, but it must be kept in mind that VOC analysis has several aspects, which set limitations for the amount of the samples. First of all, the measurement of one sample is very time consuming. In our system described later, one analysis took more than an hour and next to collected samples also standards and samples needed for the quality assurance must be measured, which further increases the sample load and the time needed for measuring the field samples. The second restriction is the stability of the target compounds in the sample matrix. This can be tested before sampling, but the results of stability tests should be interpreted with precaution. The simulation of the precise sample matrix — in laboratory conditions for example — is very difficult, if not impossible. In the best case, an assumption might be made of the stability of the target compounds during a defined storage time. Therefore, for gaining the qualitatively best result, the samples should be analysed as soon as possible after the sampling, which again limits the total amount of samples. Considering the total sample load of this three-day sampling campaign, including the emission samples, control samples and the samples needed for quality assurance, the maximum sample amount was reached, which still was considered to be analysed in acceptable time-frame after the sample collection. The maximum storage time for chloromethane samples was three weeks, which was the time the compound

stayed stable on the adsorbent material in the storage experiment.

### Sampling system

The sampling system (Fig. 2) consisted of a moisture trap: a plastic tube (229 mm × 38 mm) with aluminium ends filled with  $Mg(ClO_4)_2$  granules, a stainless steel adsorbent tube (178 mm, OD 1/4'', Gerstel), a regulation valve (Swagelok®), a thermal flow meter with totalisator (Profimess GmbH, Bremerhaven, Germany) and a membrane pump (KNF Neuberger GmbH, Freiburg, Germany). Different parts of the system were connected with Silcosteel® coated stainless steel tubing (1/8'') and gas-tight Swagelok®-fittings or Tygon®-tubing in places where more flexibility was needed. The tightness of the fittings was tested in the laboratory before sampling. The adsorbent bed was made of a combination of three adsorbents: Tenax TA and two types of Carboxen (all from Supelco, Bellefonte, PA, USA).

### Analytical methods

The samples were analysed using thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). Our analytical setup consisted of a thermal desorption system 1 (TDS 3) and a cold injection system (CIS) (both Ger-

stel GmbH & Co. KG, Müllheim an der Ruhr, Germany) combined with a GC (Agilent series 6890N) and a mass selective detector (Agilent series 5975B). The GC was equipped with a GasPro PLOT column (30 m × 0.32 mm, J&W Scientific) and programmed with the following temperature programme: 40 °C held 5 min, heated to 220 °C (rate 6 °C min<sup>-1</sup>) held 10 min, and finally heated to 240 °C (rate: 25 °C min<sup>-1</sup>) and held 10 min. The GC was operated in the constant flow mode with a carrier gas flow of 2.7 ml min<sup>-1</sup>. The compounds were identified according to their retention times and mass spectra. For quantification of the halomethanes, one-point calibration with single compound calibration standards (CH<sub>3</sub>Cl, CH<sub>3</sub>Br or CH<sub>3</sub>I, Linde Gas, Germany) was used. The calibration standards were measured daily at least 3 times, and the measurements showed a relative standard deviation of less than 5%.

### Calculation of chloromethane fluxes

The fluxes were calculated with the following equation:

$$\text{Flux} = \left[ \frac{M_T - M_T^0}{VT(1 - e^{-JT/V})} V/A \right] 60 \text{ min},$$

where  $M_T$  (ng) is the mass of chloromethane collected from the plant enclosure in the sampling time  $T$  (min),  $M_T^0$  (ng) is the mass of chloromethane collected from the enclosure without vegetation in the sampling time  $T$ ,  $V$  (dm<sup>3</sup>) is the volume of the chamber,  $J$  (dm<sup>3</sup> min<sup>-1</sup>) is the sampling flow and  $A$  is the area of the chamber base.

When the emissions were normalised to biomass, the term  $V/A$  was replaced with  $V/m$ , where  $m$  represents the dry biomass harvested from the enclosure.

This equation is valid if the following circumstances should apply inside the chamber:

1. chloromethane flux stays constant during the enclosure time,
2. emitted chloromethane is immediately distributed equally into the whole chamber volume after its liberation,
3. there is a constant laminar air flow sweeping through the chamber.

The enclosures without vegetation were located in the area without vegetation nearest to the corresponding vegetated enclosure site. In all cases, the distance between these enclosures was less than three meters. A total of five incubations without vegetation at different times of day were conducted in the course of the three days. For calculation of the fluxes we used the average of these five values. The used equation and its induction is presented in detail in the Appendix.

### Soil analyses

Two soil samples (0–20 cm) were collected under each vegetation type and soil properties were determined to obtain information on abiotic parameters most likely to affect the chloromethane production in and hydromorphological features of the soil. For the collection a steel corer was used (length: 50 cm, diameter: 8 cm). All the analyses except for TOC were conducted on the fresh surface layers of the soils, which we considered to be the most relevant horizon with regard to possible chloromethane production. Total organic carbon was analyzed from air dried surface layers. The visual characteristics of the soil cores (laminae and their colour) were recorded. The determination of soil texture was based on sensory analysis in the field, no textural analysis was conducted in the laboratory. For the laboratory analyses, the organic soil horizon was separated from the mineral soil and plant roots and small stones were removed from it. The organic soil material was then homogenized. The soil under vegetation type 1 (*S. europaea*) is here to fore referred to as soil 1 and soil under vegetation type 2 (mixed hay and grass species) as soil 2.

For pH measurements, 1 g of fresh soil was suspended in 2.5 ml of 0.01 M CaCl<sub>2</sub>, shaken by hand for several minutes and allowed to stabilize for approximately 15 min before dipping the glass electrode into the solution. For electrical conductivity (EC), a soil suspension of 1:5 (w/v) (fresh soil) in milliQ-purified water was shaken by hand and allowed to stabilize for 15 minutes prior to the measurement with a conductivity meter (CDM210, MeterLab Radiometer, Copenhagen). Both pH and electrical conductivity were analysed in triplicates.

The chloride concentration in the suspension used for the EC measurement was measured by pipetting 0.5 ml of the suspension into the analyser vial, and the analysis was conducted with an MK II Chloride Analyzer 926 (Sherwood). Manganese and iron were extracted according to Niskanen (1989). Soil samples of 2.5 g were shaken in 50 ml of ammonium oxalate (0.029 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  + 0.021M  $\text{H}_2\text{C}_2\text{O}_4$ , pH 3.3) for two hours (150 rpm) in a vertical table shaker, centrifuged, and the supernatants were filtered through filter paper (S & S, Blauband) prior to analysis. Iron and manganese concentrations in the extracts were measured with an ICP-MS (Perkin-Elmer, Elan 6000). Total organic carbon (TOC) in the air-dried sample was determined with an automatic TOC-analyzer (Shimadzu TOC-Vcph + TNM-1). For total organic carbon, iron, manganese and chloride analyses, five parallel determinations were conducted.

## Results

### Soil samples

Soil 1 (*S. europaea*) had an approximately 3.5-cm-thick surface layer with the uppermost 1 cm enriched with organic material (OM) as compared with lower parts of the layer, where the amount of sand started to increase. The layer was dark grey. The layer (3.5–7 cm) beneath the surface layer was pale yellow-brown and quite coarse in texture, and included several small stones. Right below the sandy layer, a grey clay layer began. Only the surface soil to about 20 cm depth was sampled and, therefore, the thickness of the clay layer could not be determined as it went deeper than the sampling depth. In the organic layer, the plant root growth was mostly shallow and near the soil surface. There were

very few roots in the sandy horizon and no visible roots in the clay layer.

Soil 2 (mixed vegetation) had a thicker surface layer (about 7.5 cm) rich in OM. It contained plenty of roots. The second visually distinct layer was a pale grey mixed sand/clay layer that also contained roots and appeared to have a higher water content and lower density than the clay layer in soil 1. This layer also extended beyond our sampling depth of 20 cm. The organic layer in soil 1 was thinner than in soil 2 because the recent burning of the surface vegetation had destroyed most of the decomposed organic material.

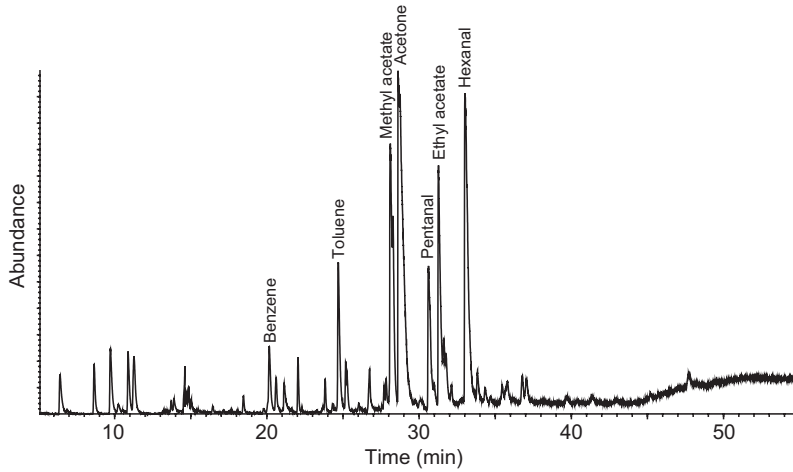
Both soils had near-neutral pH (Table 2) and can be classified as neutral chloride soils according to Siira (1984, 1985). The largest difference between the soil samples was in TOC, it being three times higher in soil 2 than in soil 1. Furthermore, in soil 2 the concentrations of chloride and iron, as well as the value of EC, were also somewhat higher than in soil 1, whereas pH was lower.

### Identified VOCs

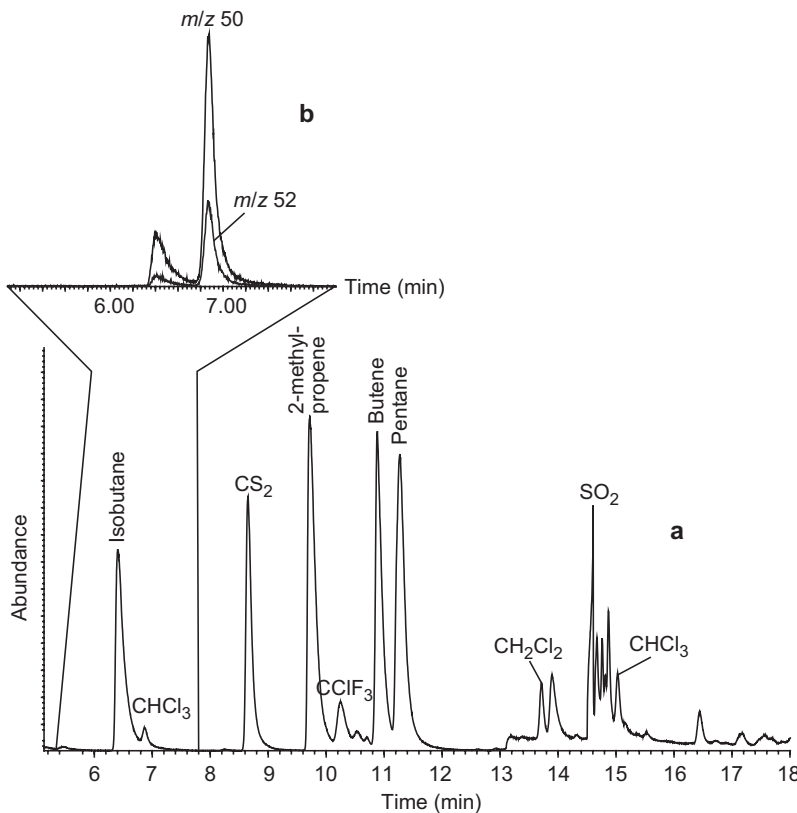
The mean temperature within the chambers on the sampling days (10–12 July 2007) was 20.6 °C and mean relative humidity was 72%. No temperature rise or humidity accumulation was observed in the majority of the incubations. The major components in the emission samples were acetone and hexanal, followed by methyl acetate, pentanal, ethyl acetate, benzene and toluene (Fig. 3). These compounds were identified by comparing their recorded mass spectra with those in the spectral library (NIST). The most abundant VOCs in our samples were isobutane, 2-methyl-propene, butene and pentane (Fig. 4). Isobutane, butane, and butene and its structural

**Table 2.** Soil parameters from the soil surface layers under the two vegetation types.

	pH	EC <sub>1:5</sub> (mS cm <sup>-1</sup> )	TOC (%)	Mn/Fe ( $\mu\text{g g}^{-1}$ )	Cl <sup>-1</sup> (mg g <sup>-1</sup> )
Soil 1 ( <i>S. europaea</i> )	6.7	1.9	3.2	1.2/11.4	2.4
Soil 2 (mixed vegetation)	5.9	3.1	11.0	0.9/16.6	3.4



**Fig. 3.** Typical chromatogram of a plant (*S. europaea*) emission sample (5–55 min). Abundance (*y*-axis) is a relative variable, therefore, no unit is given.



**Fig. 4.** (a) Magnification of the retention times from 5 to 18 min (same chromatogram as in Fig. 3), (b) extracted ion chromatogram displaying the main ion fragments (*m/z* 50 and 52) of chloromethane. Abundance (*y*-axis) is a relative variable, therefore, no unit is given.

isomer 2-methyl-propene (isobutene) were identified by comparing their retention times with the retention times of the gas standards containing butane, butene and their iso-forms ( $C_1$ – $C_4$  alkane and  $C_2$ – $C_4$  alkene minican standards, Linde Gas, Germany). Isobutane normally eluted right before chloromethane. However, in a few samples where isobutane was present in a high

concentration relative to chloromethane, partial co-elution was observed (Fig. 4a). On such occasions, quantitation was conducted with the help of the extracted ion chromatograms (Fig. 4b). We also observed some sulphur-containing compounds in the emission samples. Carbon disulphide ( $CS_2$ ) and sulphur dioxide ( $SO_2$ ) were present large amounts, but dimethyl sulphide and



methanethiol were also often detected.  $\text{SO}_2$  is an artefact generated by the adsorbent materials during the desorption step. It was also detected in the blank runs, where only the conditioned adsorbent tubes were analyzed. Several halogenated  $\text{C}_1$  and  $\text{C}_2$  compounds could be detected in the collected gas samples,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_3\text{F}$  (CFC-11) and  $\text{CH}_3\text{Cl}$  being the most abundant.

### Chloromethane emission

The flux measurements had a relatively large gap in the *S. europaea* sites between 08:00 and 14:00 local time (Table 3). The highest flux value for *S. europaea*,  $841 \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$  was observed between 14:00 and 16:00. From the mixed vegetation the highest flux value,  $562 \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$ , was recorded in late afternoon between 16:00 and 18:00. The lowest chloromethane fluxes occurred between evening and early morning and followed a similar trend in both vegetation types (Table 3 and Fig. 5).

The net fluxes showed relatively large differences in magnitude and diurnal distribution between the different sites of the same vegetation type (Table 3 and Fig. 5a–b). In *S. europaea* site 1, the net emission fluxes varied from 63 to  $865 \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$  and in *S. europaea* site 2 from 480 to  $817 \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$ . In the mixed vegetation site, the net emissions were between

0–365 and 292–759  $\text{ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$  for sites 1 and 2, respectively. These discrepancies between the sites became smaller when fluxes were normalized to dry biomass for *S. europaea* (Fig. 5a), but remained relatively wide for the mixed vegetation type (Fig. 5b).

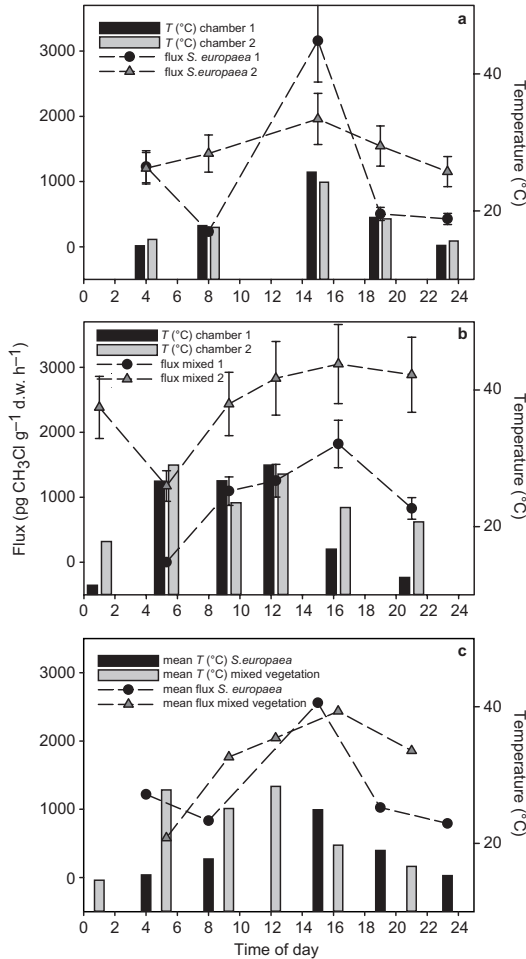
*Salicornia europaea* had a higher tissue water content (Table 4) than the mixed vegetation species, which diminished the emission values when the fluxes were related to the fresh biomass. On the other hand, *S. europaea* sites possessed a higher above-ground biomass (Table 4), which explains why they had higher area-normalised fluxes than the mixed vegetation sites. The mean flux values normalised to dry biomass showed almost no differences between the two vegetation types (Fig. 5c). Our mean flux values were based on the averages taken from the two different sites of each vegetation type. The number of observations is too small to give statistically valid results, which is a common problem in chamber-based emission measurements.

As there was no apparent difference between the two vegetation types concerning their emission rates, the both types were taken as a one group (all species) in calculating the daily flux from the study area. All observation ( $n = 21$ ) were divided into two groups: (1) background emission fluxes recorded 00:00–04:00 and 18:00–24:00 ( $n = 17$ ) local time and (2) maximum emission fluxes recorded 14:00–18:00

**Table 3.** Net chloromethane fluxes ( $\text{ng m}^{-2} \text{ h}^{-1}$ ) from plant incubations.

Date	Time	<i>S. europaea</i> 1	<i>S. europaea</i> 2	<i>S. europaea</i> average
11 July	03:00–05:00	337	502	419
11 July	07:00–09:00	63	596	329
10 July	14:00–16:00	865	817	841
10 July	18:00–20:00	138	644	391
10 July	22:00–24:00	117	480	299
		Mixed 1	Mixed 2	Mixed average
12 July	00:00–02:00		593	
12 July	04:00–06:00	0*	292	144
12 July	08:00–10:00	220	606	413
11 July	12:00–14:00	252	705	478
11 July	16:00–18:00	365	759	562
11 July	20:00–22:00	166	718	442

\* Calculated flux was slightly negative. As only positive fluxes were considered possible (no mechanism is known for degradation of chloromethane in plants), the positive flux is given as 0 for this measurement.



**Fig. 5.** Dry biomass-normalised chloromethane fluxes and corresponding average temperatures in the chambers during the incubations. (a) *S. europaea* sites, (b) mixed vegetation sites, (c) mean emission from each vegetation type. In plots a and b the error bars represent the analytical uncertainty of  $\pm 20\%$  of the GC-MS-system used for analysing the samples. Note the different scales.

( $n = 4$ ). The mean fluxes ( $\pm$  standard deviation) were  $378 (\pm 241)$  ng m<sup>-2</sup> h<sup>-1</sup>,  $1330 (\pm 863)$  pg g<sup>-1</sup> (d.w.) h<sup>-1</sup> and  $701 (\pm 228)$  ng m<sup>-2</sup> h<sup>-1</sup>,  $2496 (\pm 704)$  pg g<sup>-1</sup> (d.w.) h<sup>-1</sup> background and maximum group, respectively. It was assumed that the background mean flux represented the mean flux in 20 hours of the day and maximum fluxes the mean flux in four hours of a day. The daily flux was calculated as a sum of the background flux and the maximum flux times their appearance time in hours, by dividing this with 24 hours we gained the weighted means. The weighted means ( $\pm$  standard errors) for all species were  $432 (\pm 25)$  ng m<sup>-2</sup> h<sup>-1</sup> and  $1524 (\pm 105)$  pg g<sup>-1</sup> (d.w.) h<sup>-1</sup>, resulting in the daily fluxes of  $10.36 (\pm 0.60)$   $\mu$ g m<sup>-2</sup> d<sup>-1</sup> and  $36.58 (\pm 2.54)$  ng g<sup>-1</sup> (d.w.) d<sup>-1</sup>.

## Discussion

### Soil

In the soil samples the clay layer starting at a depth of 7–8 cm had a uniform pale grey colour and showed no visual signs of oxic conditions, e.g. any red-brown colour from oxidised iron. It is therefore probable that the subsoils stay anoxic because of the high water level due to the nearness of the shoreline and poor penetration of oxygen-containing water through the compact clay layer.

According to Keppler *et al.* (2000), the main properties of soils influencing abiotic chloromethane production are (i) soil chloride concentration, (ii) organic carbon content, and (iii) reducible iron (Fe III) concentration. Also, the

**Table 4.** Biomass water content and mean above-ground biomass.

	Fresh biomass (g)	Dry biomass (g)	Water content (%)	Mean biomass (above ground) (kg m <sup>-2</sup> )	
				Fresh weight	Dry weight
<i>S. europaea</i> 1	27.2	2.6	90.4		
<i>S. europaea</i> 2	40.4	4.0	90.2		
<b>Mean</b>	33.8	3.3	90.3	3.6	0.4
Mixed 1	5.8	1.9	67.0		
Mixed 2	10.0	2.4	76.7		
<b>Mean</b>	7.9	2.1	72.8	0.8	0.2

ambient environmental conditions like temperature, soil moisture and pH, and the chemical composition of the soil OM play major roles. In the present study, the soils differed to some extent in pH, EC and Cl concentration. pH was lower in soil 2 owing to its high content of OM known to contain humic and fulvic acids. It is likely that the higher EC in soil 2 was attributable primarily to the higher Cl<sup>-</sup> concentration caused by flooding of brackish water, although the dissolved organic acids may also have had some effect. In the absence of particle size data (bulk density) it is difficult to estimate which one of the soils was actually more saline.

In our opinion, the major factor determining the vegetation type in the experimental location was burning that cleared the patches (soil 1) of other vegetation and gave an advantage to the pioneer species *S. europaea*, rather than any chemical or physical differences between the soils. Soils possess a variety of biological components that either produce or degrade chloromethane. Chloromethane production has been reported for ectomycorrhizal fungi (Redeker *et al.* 2004) and wood-rotting fungi (Watling and Harper 1998). On the other hand, several bacterial strains have been found to be capable of using chloromethane as a sole carbon source (reviewed in McDonald *et al.* 2002 and Schäfer *et al.* 2007). Thus, soil can function as a sink or a source for chloromethane and hence forms a highly complex biological system, which renders it challenging to assess the possible abiotic generation of volatile compounds. However, soil biological processes were beyond the scope of this study.

In the light of the measured soil parameters, abiotic chloromethane formation would be more likely in soil 2, because of the higher content of OM, chloride and redox-sensitive elements (iron). Abiotic chloromethane production might therefore be a factor affecting the flux data for mixed vegetation sites, especially as all the soil controls were measured on soil 1, because no unvegetated patch were available at the sampling site 2. Thus, the chloromethane fluxes for the mixed vegetation sites might be overestimated due to underestimation of the contribution from soil.

## Volatile non-halogenated organic compounds

The mixed adsorbent bed used was designed to trap a wide range of VOCs (C<sub>1</sub>–C<sub>4</sub>), but our special interest was focused on halogenated organic species. Four different halogenated methanes were detected. Dichloromethane and chloroform are both widely-used solvents, but have also natural sources (Laternus *et al.* 2002, Cox *et al.* 2004). Chloroform emission is often recorded from areas where chloromethane is also emitted (Dimmer *et al.* 2001, Cox *et al.* 2004), but it shows a different kind of emission pattern. Hellén *et al.* (2006a) found boreal forest floor to emit chloroform at a rate of 100–800 ng m<sup>-2</sup> h<sup>-1</sup>, but they did not detect any chloromethane formation. These observations suggest that chloroform is derived from different processes than chloromethane.

In our samples, acetone and hexanal were the predominant VOCs. Acetone is one of the most abundant non-methane hydrocarbons found in the atmosphere in remote areas and has multiple natural and anthropogenic sources (Singh *et al.* 1994). Shade and Goldstein (2006) detected a seasonal variation in acetone concentrations in Californian rural air, indicating that this substance is mostly of biogenic origin. Hexanal is derived from decay of fatty acids from biological material. For example, Heiden *et al.* (2003) found C<sub>6</sub>-products, including hexanal, to be the main oxygenated volatile organic compounds from a variety of plant species. They suggest the oxidation of linoleic (18:2) and linolenic (18:3) acids by lipoxygenase to be the probable source for these compounds.

Isoprene (2-methyl-1,3-butadiene) and monoterpenes are the most common biogenic VOCs emitted by vegetation, especially trees. We could not detect isoprene in our samples. This is probably due to the unsuitability of our adsorbent system. Isoprene has been observed to break down rapidly after sampling in Carboxen-type adsorbents (Dettmer *et al.* 2000). It is also possible that the meadow vegetation does not emit isoprene, because not all plant species have the gene encoding isoprene synthesis (Sharkey and Yeh 2001).

## Chloromethane fluxes

### Plant material

In our study, relatively large discrepancies remained between the chloromethane emission levels among the different sites of the mixed species after normalising to dry biomass. For *S. europaea*, the differences between the two sites became clearly smaller when normalised to biomass. The differences in the fluxes from the mixed vegetation sites are partly due to variation in the relative coverage of different plant species between the two sites. Halomethane flux rates have been found to strongly depend on the species (Manley *et al.* 2007, Yokouchi *et al.* 2007). There might also be true differences between the emissions rates from plant individuals of the same species. In fact, high intra-species variations have been detected in tropical plants (Yokouchi *et al.* 2007) and salt marsh vegetation (Rhew *et al.* 2002). The amount of biomass of a given species is therefore not solely responsible for variations in the extent of the emissions, but the developmental stage and overall health of the individual plant might also contribute to differences in emissions. The correlation between the flowering of plants and halomethane (not necessarily chloromethane) emissions found by Manley *et al.* (2007) suggests that the plant age and developmental status are key factors in regulation of the amount of liberated gas.

In our study, the *S. europaea* sites showed slightly higher rates than the mixed sites when the CH<sub>3</sub>Cl fluxes were based on the area, but slightly lower rates when based on biomass. Overall, the differences in CH<sub>3</sub>Cl emission rates between the two vegetation types were not substantial, in comparison with over 100-fold differences between Californian saltmarsh species (Table 1) found by Manley *et al.* (2007). The mean area-based net flux (= daily mean divided by 24) recorded in our study was 432 ng m<sup>-2</sup> h<sup>-1</sup>. It is in the same range as the fluxes obtained by Cox *et al.* (2004) and Dimmer *et al.* (2001) and those reported by Rhew *et al.* (2001) for a *Larrea tridentata*-dominated site and by Varner *et al.* (1999) for a rich fen. The fluxes reported for *Atriplex canescens* (Teh *et al.* 2008), *Spartina* and *Salicornia* (Manley *et al.*

*et al.* 2007) as well as for a poor fen (Varner *et al.* 1999) were approximately two times higher than our daily maximum value. The daily average values obtained by Manley *et al.* (2007) were all recorded between 09:00 and 14:00, which partly overlaps the window of time wherein we found the maximum emissions. Hence, the comparison of the maximum values appears to be appropriate.

Only three studies listed in Table 1 report emission values from which the influence of soil emissions is deducted, all other studies give total emission values that include soil emission. Moreover, only a few studies (Dimmer *et al.* 2001, Rhew *et al.* 2001, 2000) took daily variations into account. These facts complicate comparisons between the emission values of different studies.

The subtropical biomass-based emissions rates (Table 1) are three orders of magnitude larger than our mean biomass-normalized rate of 1.52 ± 0.11 ng g<sup>-1</sup> (d.w.) h<sup>-1</sup> for all species. This discrepancy derives from the differences in the vegetation composition and environmental parameters e.g. temperature, salinity and insolation. Chloromethane formation is a characteristic feature probably regulated at the genus level in plants (Yokouchi *et al.* 2007). Perhaps the magnitude of emission is also controlled at the genus level. The two *Salicornia* (*europaea* and *virginica*) species have emission rates of the same magnitude, despite the differences in their geographic settings. There is a 3-fold difference in the dry biomass-normalised fluxes of *Salicornia* between our study and that of Manley *et al.* (2007). Also, different *Frankenia* species have shown about 2-fold differences in their dry biomass-normalised emission rates (*F. salina*: 1367–1494 ng g<sup>-1</sup> h<sup>-1</sup> (Rhew and Abel 2007) and *F. grandifolia*: 582 ng g<sup>-1</sup> h<sup>-1</sup> (Manley *et al.* 2007). This might be caused partly by methodological differences in the calculation of the daily mean fluxes and partly by differences between the sites. As already mentioned, it is difficult to compare the emission rates of *S. bigelovii* (Rhew *et al.* 2000) with other data, because the study neither differentiated between soil- and vegetation-derived emissions nor presented biomass-normalized rates. Compared with our data, the most similar biomass-normalised emis-

sion rates have been reported for the short grass steppe species *A. canescens* (Teh *et al.* 2008) and coastal salt marsh species *S. virginica* (Manley *et al.* 2007).

### Environmental parameters

Halomethane production by plants has been shown to be an enzymatic process (Wuosmaa & Hager 1990, Manley 2002). However, in addition to plant species and physiological characteristics, environmental factors also regulate emission rates. Halomethane emissions have been found to correlate with air temperature and the amount of photosynthetically active radiation (Dimmer *et al.* 2001, Rhew *et al.* 2002, Saito and Yokouchi 2007). Manley *et al.* (2007) point out the difficulty in field studies in differentiating between effects caused by changes in the light intensity and those caused by temperature, as these two factors normally correlate strongly. During the sample and control incubations, we monitored temperature and the relative humidity in the chambers, because they are the major factors affecting enzyme activity in plant cells (Heldt 2004). In most cases, temperature in the chamber correlated quite well with the amount chloromethane emitted [linear regression:  $r^2 = 0.63\text{--}0.98$  ( $n = 5$  or  $6$ )]; only the mixed vegetation site 2 had a poor correlation ( $r^2 = 0.45$ ,  $n = 6$ ) between these two parameters.

Salinity has been thought to be an important factor in halomethane production (WMO 2007), but it seems not to directly correlate with emission rates (Yokouchi *et al.* 2002, Manley *et al.* 2007). Still, soil salinity is an important environmental parameter as it has a strong influence on the type of vegetation that grows in a given ecosystem. Investigations made in different kinds of shrubland (Rhew *et al.* 2001) and grassland (Rhew and Abel 2007, Teh *et al.* 2008) ecosystems reveal a close relationship between the net chloromethane production and the halophytic plant species present. The highest chloromethane net emission rates measured from dry grassland have been obtained from a hypersaline site (Rhew and Abel 2007).

Interestingly, in dryland ecosystems the water content in the soil seems to be an impor-

tant factor controlling the chloromethane net emission and uptake. In the studies of Rhew *et al.* (2001), Rhew and Abel (2007) and Teh *et al.* (2008), chloromethane net emissions occurred only during dry seasons (soil water content  $\leq 10\%$ ). Water content is of crucial importance in controlling the biological activity in the soil. Soil bacteria can degrade chloromethane either under oxic or anoxic conditions, but in general aerobic degradation processes are considered to be more efficient and faster than anaerobic processes. Further studies are needed to determine if there is a moisture regime optimal to microbial oxidation.

There might be also a certain temperature and salinity "threshold" in the northern ecosystems for chloromethane production. For example, Dimmer *et al.* (2001) could detect relatively high halomethane emission rates from Irish peatlands and forest floors, but Hellén *et al.* (2006a) could not detect any emissions from the Finnish inland peatland or the coniferous-forest floor. This suggests that the salinity in inland sites in Finland was probable not high enough to initiate halomethane formation. In this study, performed on a coastal area of the Baltic Sea, we could detect at least chloromethane emissions. Thus, the halogenated hydrocarbons measured by Hellén *et al.* (2006b) in the air of urban and residential areas in southern Finland may originate in areas affected by brackish water. Hellén *et al.* (2006b) modelled the measured halogenated hydrocarbons as having their origin in a distant source, but the type of this source could not be identified. A temperature threshold might have been the reason why Rhew *et al.* (2007) could record almost no halomethane emission from a tundra coastal site in Alaska, where the salinity is most probably at least the same or higher than on the Baltic Sea coast in Finland.

### Geographic location

When considering the  $\text{CH}_3\text{Cl}$  emissions from vegetation, the (bio)geographic location of the sampling site is of a paramount importance. It is this factor which mainly determines the vegetation type by dictating the length of the growing season, the temperature and the diurnal light

conditions. Halophytes on coastal wetlands and inland grass- and shrublands at higher latitudes may have chloromethane production rates of global relevance. Estimating the magnitude of these sources is hindered by the lack of field data and uncertainties in the estimations of the global coverage of these ecosystems. Our sampling site was located in the southernmost part of the boreal zone, which has a substantially lower net primary production rate than the tropics (Field *et al.* 1998). The relationship between biomass production rate and the emission of chloromethane, not investigated so far, should be studied in order to adjust the global budget of HVOCs.

### Representativeness of the collected data

Four vegetated plots were sampled using chambers with basal area of 0.0095 m<sup>2</sup> during three days in the first half of July 2007. The collected dataset is relatively limited in space and time.

The sampling days were situated in the middle of the thermal growing season in this climatic zone, which is the time of the year having the highest mean temperature. The mean temperature of July in the years 1971–2000 was 16.9 °C (see [www.fmi.fi/saa/tilastot.html](http://www.fmi.fi/saa/tilastot.html)) in this region. Our sampling days were somewhat warmer, than the long-term average, but not exceptional so for July. Currently, there exists controversial information about the seasonal emission patterns of monohalomethanes. The study of Manley *et al.* (2006) recorded monohalomethane emissions from a Californian saltmarsh region for 1.5 years, but could not find a distinct seasonal emission pattern in the region. Cox *et al.* (2004) however found the largest chloromethane net emissions during the spring and summer time. These studies were performed in regions with very different climatic conditions as the investigated area in our study. It would be logical to expect seasonality in the vegetation derived emissions of the boreal coastal meadows due to the deciduous nature of their plant species and the harsh (snow coverage, low temperatures) weather conditions of the non-growing season in this area.

As mentioned before, Manley *et al.* (2006) noticed that flowering was coinciding with maximal emissions of chloromethane in some plant

species. In the time of our measurements also some of the sampled species (e.g. *Glaux maritima* and some of the *Carex* species) were flowering. This fact together with the relatively high temperatures in the sampling days leads to the conclusion that our results are probably in the higher end of the scale for chloromethane emissions during the growing season of 2007. The vegetation of the study area showed species, which are typical at the brackish water affected coastal region of this part of the Baltic Sea (Siira 1985).

A better picture of the emissions would be gained, when more enclosures could be used and several sampling campaigns in different years and times of year could be undertaken. As our sampling location was very remote lacking the advantages of a continuously occupied research station or an institute (storage possibilities, energy, personnel, etc.), the sampling campaign was bound with a considerable logistic effort and costs. Considering this we had to settle for one campaign during the growing season. Despite of the limitation of our dataset, it still provides new and valuable information from an area, which has not been investigated in this context before.

Next to limitation in space and time our results might also be biased because of the missing information about the chloromethane emissions and degradation of the different soil types, so that only indirect estimations of the contribution of the investigated soils could be made.

### Conclusion

The observed chloromethane fluxes from a boreal coastal meadow were  $10.36 \pm 0.60 \mu\text{g m}^{-2} \text{d}^{-1}$ , and  $36.58 \pm 2.54 \text{ ng g}^{-1} (\text{d.w.}) \text{d}^{-1}$  for the boreal coastal meadow vegetation. These emissions rates were similar to those obtained from other coastal ecosystems. No significant differences were detected between the emission rates of the vegetation types. The emission rates from both vegetation types varied strongly among different times of day (2–14-fold differences between the maximum and minimum rates). These variations were mostly well-correlated with changes in air temperature.

Chloromethane emission data from boreal coastal vegetation are scarce and, to our knowl-

edge, the current study is the first to report such data. Its results suggest that boreal coastal areas might be a considerable source of chloromethane, contributing substantially to the atmospheric concentration on the local and perhaps also on the global level. Further investigations should be made to discover the actual extent of this source and the mechanisms controlling the emissions. More information on the influence of soil parameters and especially of soil biology on chloromethane formation and degradation is needed. Also the seasonal behaviour of the emissions needs to be elucidated.

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## Appendix: Calculation of the emission fluxes

The design of our closed chamber system (Fig. 2) was somewhat different from the design of a traditional closed chamber. The constant sampling causes a steady flow through the chamber. Furthermore, the back flow of chloromethane free air dilutes the concentration of the target compound inside the chamber. After the enclosure of a plant in the chamber, the time-dependent mass density of chloromethane  $\rho \rightarrow \rho(t)$  in the chamber depends on the emission flux of chloromethane from the plant  $Q$  and the air flux through the chamber  $J$ . We assume instantaneous mixing, a constant source flux  $Q$ , and a constant air flux  $J$  during the measurement period. We denote the volume of the chamber by  $V$  and define  $q = Q/V$  and  $j = J/V$ . The change in  $\rho$  is then described by an inhomogeneous first order linear differential equation

$$\rho'(t) = q - \rho j \quad (\text{A1})$$

with the initial condition  $\rho(0) = \rho_0$ .

The solution of this differential equation is

$$\rho(t) = \rho_0 e^{-jt} + \frac{q}{j(1 - e^{-jt})} \quad (\text{A2})$$

where  $q/j$  is the steady state mass density of chloromethane in the chamber which is reached after a sufficiently long waiting time.

The air at the entrance of the trap contains chloromethane with a density  $\rho(t)$  provided that the volume of air contained in the tube connection between the chamber and the trap is small as compared with the volume of air sampled during the measurement. In this case, the mass of chloromethane absorbed in the trap per unit time is  $m(t) = \rho(t)J$ . The mass of chloromethane  $M_T$  collected on the absorbent during the sampling time  $T$  is then obtained by



$$M_T = \int_0^T m(t) dt = J \int_0^T \left[ \rho_0 e^{-jt} + \frac{q}{j(1-e^{-jt})} \right] dt$$

The calculation of the integral yields

$$M_T = V \left[ qT + \left( \rho_0 - \frac{q}{j} \right) (1 - e^{-jT}) \right]$$

In a reference sample with  $q = 0$ , we collect the mass

$$M_T^{(q=0)} = \rho_0 V (1 - e^{-jT})$$

From the difference  $M_T - M_T^{(q=0)}$  that is measured in the field experiment, we directly obtain the emission flux  $Q$ :

$$Q = \frac{(M_T - M_T^{(q=0)})}{T - \frac{1}{j(1-e^{-jT})}} \quad (\text{A3})$$