




RESEARCH ARTICLE

# Physiological reactions in plants visualized by $^{14}\text{C}$ : The impact of sea spray on radiocarbon analyses of terrestrial plants in coastal regions quantified by a greenhouse study

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## Abstract

Marine aerosols can enter the terrestrial environment via sea spray which is known to affect the stable isotope fingerprint of coastal samples (plants, animals/humans), including  $\delta^{13}\text{C}$ . However, the impact of sea spray on  $^{14}\text{C}$  dating of terrestrial organisms at coastal sites has not been investigated so far. Besides a direct effect, sea spray is accompanied by physiological effects, e.g., due to salinity. In an artificial sea spray experiment in the greenhouse, the effect of sea spray on  $^{14}\text{C}$  in plant tissue was investigated. Beach grass was sprayed with mineral salt solutions containing only traces of NaCl or with brackish water from the Schlei inlet or the Baltic Sea. These plants should give a  $^{14}\text{C}$  signal close to the modern atmospheric  $^{14}\text{CO}_2$  composition. However, three treatment groups showed variable radiocarbon concentrations. Plants sprayed with water from the Schlei inlet, Baltic Sea water, or with a mineral salt solution with very high  $\text{HCO}_3^-$  concentration are depleted in  $^{14}\text{C}$  content relative to contemporary atmospheric composition. While  $\delta^{13}\text{C}$  reflects physiological effects in the plants, caused either by salinity (NaCl) or  $\text{HCO}_3^-$  stress, resulting in decreased discrimination against  $^{13}\text{C}$ , the uptake of high amounts of  $^{14}\text{C}$  (ca. 53–67%) from DIC (dissolved inorganic carbon) partly masks the underlying physiological reactions, as is visible in the radiocarbon signature of the plant tissues. This preliminary study indicates that sea spray effects on plant tissue could potentially influence faunal tissue  $^{14}\text{C}$  composition at coastal sites. Further research is required to better understand the observed reservoir effect.

## 1. Introduction

The stable isotope composition of terrestrial matter (environmental samples, animals, humans) at coastal sites can be distinctly affected by sea spray aerosols. Seawater and sea spray aerosols contain a variety of different cations and anions, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{SO}_4^{2-}$  (e.g., Bates et al. 2012; Keene et al. 2007; Wright and Colling 1995b). Marine aerosols, entering the terrestrial environment via sea spray, can cause a shift in the isotope composition of biological tissues towards a seemingly marine isotope signature, masking the terrestrial isotopic fingerprint.

Besides a direct sea spray effect, caused by the uptake of isotopically enriched ions of marine origin (e.g., Clementz et al. 2006; Clementz and Koch 2001; Hobson 1999; Koch 2007; Mook 1971; Nehlich

2015), physiological and biochemical reactions in the plants can cause associated indirect sea spray effects due to discrimination caused by, e.g., salinity stress. These physiological reactions are visible in the stable isotope signature of plants, including  $\delta^{13}\text{C}_{\text{cellulose}}$ ,  $\delta^{18}\text{O}_{\text{cellulose}}$ ,  $\delta^{18}\text{O}_{\text{sulfate}}$ ,  $\delta^{34}\text{S}_{\text{sulfate}}$ ,  $\delta^{34}\text{S}_{\text{organic S}}$ , and  $\delta^{34}\text{S}_{\text{total S}}$  (Ellsworth and Sternberg 2014; Göhring et al. 2023a, 2023b; Krouse 1989; Liu et al. 2017; O’Leary 1981; Sternberg et al. 1991; Trust and Fry 1992; Yakir et al. 1990). Physiological effects can partly overlay or even mask the actual sea spray effect, making it difficult to distinguish between isotopic shifts caused by the (direct) sea spray effect and those caused by associated physiological (indirect) effects (see below).

Atmospheric  $\text{CO}_2$  taken up by plants during photosynthesis is used for a variety of metabolic pathways, such as gluconeogenesis or the Krebs cycle (see, e.g., Poschenrieder et al. 2018). However, plants can also take up  $\text{CO}_2$  (aq.) as well as dissolved  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$ .  $\text{CO}_2$  and  $\text{HCO}_3^-$  can be reversely interconverted ( $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ ) by carbonic anhydrases (see, e.g., Tiwari et al. 2005). As has been demonstrated previously,  $\text{HCO}_3^-$  cannot only be taken up via the roots of the plants but also via their leaves (Bedri et al. 1960; Göhring et al. 2023a; Overstreet et al. 1940; Poschenrieder et al. 2018; Rasmussen et al. 2013; Schäfer 1988; Stringer and Kimmerer 1993; Zamanian et al. 2017). Marine-derived  $\text{HCO}_3^-$ , which constitutes about 90% of inorganic carbon in the seawater (Poschenrieder et al. 2018), could, thus, potentially enter plant tissues via sea spray. Under controlled greenhouse conditions, the sea spray effect at the Baltic coast caused an enrichment in  $^{13}\text{C}_{\text{cellulose}}$  by about 6‰ as quantified by Göhring et al. (2023a). This shift is not only resulting from the uptake of  $\text{HCO}_3^-$  of marine origin, enriched in  $^{13}\text{C}$  (Craig 1953; Mook and Vogel 1968; Poschenrieder et al. 2018; Saltzman and Thomas 2012), but also due to a physiological reactions in the plants (indirect “sea spray” effect). Salinity stress has a distinct effect on  $\delta^{13}\text{C}_{\text{cellulose}}$  due to stomatal closure. Reduced stomatal conductance leads to a decreased discrimination against  $^{13}\text{C}$  and, thus, results in less negative  $\delta^{13}\text{C}$  values (Göhring et al. 2023a, 2023b; McCarroll and Loader 2004; Roden et al. 2005; Zhang et al. 2019). Similarly, high  $\text{HCO}_3^-$  stress, caused by a very high concentration of  $\text{HCO}_3^-$ , results in stomatal closure (see, e.g., Gao et al. 1998; Mukhtar et al. 2016; Poschenrieder et al. 2018), also affecting  $\delta^{13}\text{C}_{\text{cellulose}}$  (Göhring et al. 2023a).

Radiocarbon dating of archaeological remains from coastal sites may need to be corrected for a marine reservoir age as the marine reservoir is depleted in  $^{14}\text{C}$  activity due to pre-aged water mixture. Marine organisms usually reflect both the actual  $^{14}\text{C}$  decay and the reservoir  $^{14}\text{C}$  activity due to isotope uptake via the food chain. The so-called reservoir  $^{14}\text{C}$  age  $R(t)$  describes the age offset between the marine reservoir and the atmosphere. For regional differences, caused by different oceanographic conditions, a so-called  $\Delta R$  was defined, which accounts for the offset between regional and global ocean apparent  $^{14}\text{C}$  ages (Stuiver and Braziunas 1993). For the Baltic Sea, for example, Fischer and Olsen (2021) determined a marine reservoir age of  $273 \pm 18$   $^{14}\text{C}$  years ( $\Delta R = -234 \pm 61$  years). This is younger than the (pre-bomb) global marine reservoir effect of about 585  $^{14}\text{C}$  years, with a regional  $\Delta R$  of  $-140$  years for the Western Baltic (marine reservoir age:  $585 - 140 = 445$   $^{14}\text{C}$  years; CALIB rev. 8, Stuiver and Reimer 1993; Heaton et al. 2023, 2020).

By consuming marine food sources, e.g., fish, the marine isotope signal could be transferred to the terrestrial consumer, e.g., humans, via the food chain. However, the impact of uptake of dissolved inorganic carbon (DIC) of marine origin, i.e.,  $\text{H}^{14}\text{CO}_3^-$ , on the radiocarbon signature of plants has so far not been investigated. Such a linkage could potentially affect the  $^{14}\text{C}$  signature of humans either through direct consumption of the plants or by consuming, e.g., the meat of herbivores which in turn are directly or indirectly influenced by the plant sources affected by sea spray. A marine impact by consuming plants influenced by sea spray would, however, not be visible in the  $\delta^{13}\text{C}_{\text{collagen}}$  or  $\delta^{15}\text{N}_{\text{collagen}}$  values of consumers, which reflect the protein sources in their diet (e.g., Johansen et al. 1986; Richards et al. 2006; Richards and Hedges 1999; Schoeninger and DeNiro 1984; Schoeninger et al. 1983). The latter would (correctly) indicate terrestrial protein sources even though an individual or its diet was affected by sea spray (see Göhring et al. 2018, 2020).

This study complements an earlier published study focusing on the stable and radiogenic isotope composition ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{34}\text{S}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) of plants grown in a greenhouse and treated with an artificial



**Figure 1.** Map indicating the sampling locations for the spray water (HB = Haithabu (G-5), FE = Fehmarn (G-6)) as well as the greenhouse of the Biocenter of the LMU Munich. Google Earth Pro, Google 2022, <http://www.earth.google.com>, 12/14/2015, 51.327532 °N, 10.271728 °E, eye altitude 1808.12 km.

sea spray (Göhring et al. 2023a). Here, we examine the sea spray effect on the radiocarbon composition of these plants.

## 2. Material and methods

### 2.1 Greenhouse experiment

European beach grass (*Ammophila arenaria*, L.; Jelitto Staudensamen GmbH, Schwarmstedt, Germany) was grown in planters on a mixture of lawn sand and lawn soil (ratio 1:7; Floragard GmbH, Oldenburg, Germany), prepared for all treatment groups (see below), in the greenhouse of the Biocenter of the Ludwig Maximilian University Munich (Figure 1) in June (group 1) and July 2020 (group 2) and sampled end of December 2020. The plants grew under constant environmental conditions, at 20°C with a relative humidity of ca. 60%, and under long-day light conditions (0.9 klx).

Plants were watered with tap water (G-GW) about three days a week (ca. 150 mL/week). Irrigation water (tap water) was filled into a jerrycan, stored in the greenhouse chamber. Munich tap water mainly originates from the Mangfall as well as Loisachtal Valley. Artificial sea spray treatment (ca. 2.5 mL/week) started two weeks after sowing. At this time, germlings reached a height of about 1.5 to 2.0 cm. The used amount of spray water was just enough to result in a sufficient moistening of the leaves, thus simulating the effect of sea spray aerosol droplets on the leaves.

Seven treatments have to be distinguished according to the experimental setting in the greenhouse (see Table 1). Plants of group 1 (G-0, G-1, G-2, G-3) were sprayed with mineral salt solution, prepared

**Table 1.** Overview of the plant, irrigation water, and spray water samples for the different treatments in group 1 and 2, respectively, including  $[Na^+]$  and  $[Cl^-]$  in irrigation water as well as  $[Na^+]$ ,  $[Cl^-]$ , salinity (psu),  $[Sr^{2+}]$ ,  $[SO_4^{2-}]$ , and  $[DIC]$ , measured as mg  $CO_2$ , in the spray water samples (see text for details). NA = not available. nd = not determinable ( $[SO_4^{2-}]$  below detection level)

Group	Sample ID	Label	Irrigation water	$[Na^+]$ mg/L <sup>a</sup>	$[Cl^-]$ mg/L <sup>a</sup>	$[DIC]$ mg/L <sup>b</sup>	Spray water	$[Na^+]$ mg/L <sup>a</sup>	$[Cl^-]$ mg/L <sup>a</sup>	Salinity psu	$[Sr^{2+}]$ µg/L <sup>a</sup>	$[SO_4^{2-}]$ mg/L <sup>a</sup>	$[DIC]$ mg/L <sup>b</sup>
1	G-0	“control 1”	Tap water (G-GW)	9.70	19.37	162.5	Tap water (G-0 = G-4)	10.47	21.04	0.04	181.82	NA	298.4
	G-3	“brackish-like”					Mineral salt solution	37.82	558.65	1.01	1494.50	446.9	309.1
	G-1	“marine-like”					Mineral salt solution	75.63	1117.30	2.02	2989.00	921.3	331.7
	G-2	“>>marine”					Mineral salt solution	189.08	2793.25	5.05	7472.50	2214.1	NA
2	G-4	“control 2”	Tap water (G-GW)	9.70	19.37		Tap water (G-0 = G-4)	10.47	21.04	0.04	181.82	NA	298.4
	G-5	“Schlei”					Schlei water	1582.15	2992.40	5.41	1314.16	446.1	125.6
	G-6	“Baltic”					Baltic Sea water	3298.47	6162.20	11.13	2457.30	786.6	79.6

<sup>a</sup>Data from Göhring et al. (2023a).

<sup>b</sup>This study.

by dissolving mineral salt (Preis Aquaristik KG, Bayerfeld, Germany) of varying ion/mineral concentrations, containing only traces of NaCl (see Table 1), in tap water. Tap water (and corresponding mineral salt solution) was restocked in the spray bottles of the treatment groups (G-1 to G-3) and control groups (G-0/G-4) on a regular basis. These treatments aim to allow quantification of the impact of different ions (e.g., bicarbonate) taken up by the plants without any associated salinity impact (in contrast to group 2). As a control, plants of G-0 (“control 1”) were sprayed with tap water only. The mineral salt solutions for G-1 to G-3 were prepared by dissolving the mineral salt in Munich tap water (identical to control G-0). The artificial “marine-like” spray water for treatment G-1 was prepared with an ion concentration (e.g.,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Sr}^{2+}$ ) comparable to seawater, but containing only a low amount of NaCl (2 g mineral salt dissolved in 500 mL tap water; see Table 1) compared to about 10556 mg/L  $\text{Na}^+$  and about 18980 mg/L  $\text{Cl}^-$  in seawater (Wright and Colling 1995a). This treatment should resemble a marine spray water without salinity, i.e., NaCl, impact. The salinity level of this treatment, based on chlorinity ( $S = 1.80655 \cdot \text{chlorinity} [\text{g/L}]$ ; see Wright and Colling (1995a)), was about 2 psu (practical salinity unit; 1 psu  $\hat{=}$  1 g/L). For comparison, the salinity of the open ocean varies between about 33 and 37 psu, while brackish water of epeiric seas like the Baltic Sea has a salinity of less than 25 psu (Wright and Colling 1995a). Similarly, the artificial “brackish-like” spray water of the treatment G-3 was prepared with a brackish-like ion solution, again with a low NaCl concentration (1 g mineral salt dissolved in 500 mL tap water; see Table 1) and a respective salinity of about 1 psu. For the plants of treatment G-2 (“>>marine”) we prepared a spray water containing an ion concentration 2.5 times higher than found in natural seawater (5 g mineral salt dissolved in 500 mL tap water; see Table 1). The  $\text{Na}^+$  concentration (189 mg/L) and the  $\text{Cl}^-$  concentration (2793 mg/L) are beyond seawater levels (see above). Accordingly, salinity levels were still low with about 5 psu.

In contrast, plants of group 2 were sprayed with salty water, containing NaCl (see Table 1), from (i) the Schlei inlet (treatment G-5; “Schlei”), sampled at the Viking Haithabu site (54.491528°N, 9.5693333°E), and (ii) with water from the Baltic Sea (treatment G-6; “Baltic”), collected at the western coast of Fehmarn (Flügger Strand; 54.452361°N, 11.004722°E) in July 2020. The spray water samples for G-5 and G-6 were stored in jerrycans (at 4°C). Similar to the control G-0, the control G-4 (“control 2”) was sprayed with tap water only. This spray water was identical to the water used for G-0. Spray water of the treatments G-5 and G-6 was naturally salty and, thus, contained elevated amounts of NaCl. The salinity for the spray water of G-5 and G-6 was about 5.4 psu and 11.1 psu, respectively (see Table 1; Göhring et al. 2023a).

The control plants G-0 (group 1) and G-4 (group 2), growing on the same soil as the plants of the other treatment groups, sprayed with tap water also used to prepare the mineral salt solutions for group 1 treatments, and irrigated with the same tap water (G-GW) as all other plants, provide the isotopic signature expected for plants unaffected by sea spray. This enables a comparison with the plants of the different treatment groups growing under artificial sea spray. In addition, the controls also reflect all potential changes over the growth period (although limited in a constant greenhouse environment), including potential changes in the atmospheric  $\text{CO}_2$  and chemical or isotopic composition of tap water, as well as the background soil signal. Moreover, while we cannot fully exclude fossil fuel effects on the greenhouse plants (see above), any such effects would also influence the isotopic signature of the control plants growing under the same atmosphere as all other plants. Hence, we assume that a deviation in the isotopic signature of the treated plants from that of the control plants is the result of the artificial sea spray.

Plants were treated with the artificial sea spray five days a week (Monday to Friday) by spraying the leaves of the plants with about 0.5 mL of spray water per planter per day. This treatment was conducted from June 2020 (group 1) or July 2020 (group 2) until the end of December 2020. For measurements, one grass blade, reflecting the whole growth period, of each treatment group was sampled (length G-0: ca. 47 cm, G-1: ca. 48 cm, G-2: ca. 42 cm, G-3: ca. 50 cm, G-4: ca. 40 cm, G-5: ca. 41 cm, G-6: ca. 45 cm). The samples were processed for further analyses as described in section 2.2.

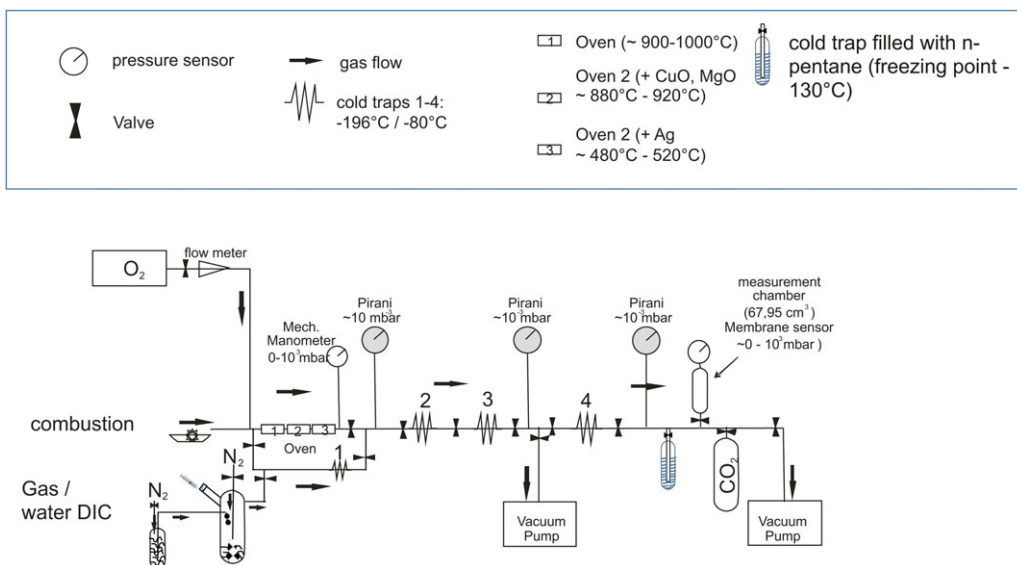


Figure 2. Illustration of the Multi-Purposed- $\text{CO}_2$ -Extraction Line (MPEL). © C. M. Hüls.

## 2.2 Laboratory analyses

This study focuses on radiocarbon measurements. The relevant parts of the laboratory analyses are presented below. The protocols for stable isotope analysis or elemental analysis of sampled plant leaves and spray as well as irrigation water samples are published elsewhere (see Göhring et al. 2023a). The radiocarbon analyses were conducted at the Leibniz Laboratory for Radiometric Dating and Stable Isotope Research in Kiel.

The sampled plant leaves were washed twice in an ultrasonic bath (Bachofer) using distilled water for 15 min each to remove surficial salts and subsequently dried in a drying oven (SALVIS, KCTS 11). Plant sample material selected for radiocarbon analysis was inspected for macroscopic contamination under the microscope. Plant material was successively treated with 1% HCl, 1% NaOH (60°C), and 1% HCl. The resulting alkali residue was combusted following Nadeau et al. (1998).

For the water samples used during the growth experiments (i.e., irrigation and spray water), a high-vacuum Multi-Purposed- $\text{CO}_2$ -Extraction Line (MPEL; see Figure 2) was used. The  $\text{CO}_2$  extraction line was conditioned by evacuation below 1 mbar, flushed three times with ultra-pure  $\text{N}_2$ , and a final  $\text{N}_2$  fill, pressured between 400–600 mbar. After water sample transfer under an ultra-pure  $\text{N}_2$  gas stream, 5 mL degassed 100%  $\text{H}_3\text{PO}_4$  was added to acidify the sample. The dissolved inorganic carbon (DIC) was stripped under a  $\text{N}_2$  gas stream (50 mL/min for about 30–40 min) as  $\text{CO}_2$ .  $\text{CO}_2$  was subsequently cryogenically collected and purified with liquid nitrogen ( $-196^\circ\text{C}$ ) and a dry-ice/alcohol slurry ( $-80^\circ\text{C}$ ) under vacuum ( $< 0.001$  mbar). The amount of  $\text{CO}_2$  was estimated by measuring the pressure of the gas in a defined volume (in mg  $\text{CO}_2/\text{L}$ ).

After graphitization of the resulting  $\text{CO}_2$  (Nadeau et al. 1997) from either combustion or DIC extraction, AMS measurements were performed with a HVE 3MV Tandetron 4130 at the Leibniz Laboratory in Kiel. The simultaneously measured isotope ratios  $^{14}\text{C}/^{12}\text{C}$  and  $^{13}\text{C}/^{12}\text{C}$  of the sample were compared with a  $\text{CO}_2$  measurement standard (Oxalic Acid II) and successively corrected for effects caused by contamination with external carbon during sample processing, determined by a double-blind test. The resulting  $^{14}\text{C}$  content of the sample is corrected for isotope fractionation and is given as  $\text{F}^{14}\text{C}$  related to the hypothetical atmospheric value in AD 1950 according to

$$F^{14}\text{C} = \frac{A_{\text{SN}}}{A_{\text{ON}}} \quad (1)$$

with the normalized specific activity of the sample ( $A_{\text{SN}}$ ) and the normalized specific activity of Oxalic Acid II ( $A_{\text{ON}}$ ), whereby the specific activity of the standard is normalized to  $\delta^{13}\text{C} = -25\text{‰}$  (Reimer et al. 2004). The conventional radiocarbon age ( $^{14}\text{C}$  age) can be calculated according to

$$^{14}\text{C} = -8033 * \ln F^{14}\text{C} \quad (\text{Stenström et al. 2011}) \quad (2)$$

The proportion of fossil carbon (fossil  $^{14}\text{C}$  (%)) in the plants can be calculated by

$$\text{fossil } ^{14}\text{C} (\%) = \left(1 - \frac{F^{14}\text{C}_{\text{plant}}}{F^{14}\text{C}_{\text{atm}}}\right) * 100 \quad (\text{Quarta et al. 2007; Varga et al. 2019}) \quad (3)$$

with  $F^{14}\text{C}_{\text{plant}}$  and  $F^{14}\text{C}_{\text{atm}}$  being the apparent  $^{14}\text{C}$  concentration in the plant samples and the contemporary atmosphere, respectively. Atmospheric  $^{14}\text{C}$  during the experiment's growth period (group 1 [G-0 to G-3]: June–December 2020, group 2 [G-4 to G-6]: July–December 2020) can be calculated to about  $F^{14}\text{C}_{\text{atm}} = 1.0048$  ( $\Delta^{14}\text{C}_{\text{atm}} = -3.6560\text{‰}$ ) for group 1 and about  $F^{14}\text{C}_{\text{atm}} = 1.0044$  ( $\Delta^{14}\text{C}_{\text{atm}} = -4.0200\text{‰}$ ) for group 2, using the Hohenpeissenberg (HPB; 47.8011°N, 11.0246°E) atmospheric  $^{14}\text{CO}_2$  dataset (Kubistin et al. 2024). The HPB atmosphere data used here are only an approximation of the atmosphere present in the greenhouse (distance between HPB and LMU Biocenter: ca. 50 km). The real atmospheric  $^{14}\text{C}$  could be different from the HPB data, also due to potential urban fossil influences. Due to controlled air flows (air filters) in the climate chamber and the suburban location of the greenhouse, this potential impact is most likely very small, even though it cannot be fully excluded. The percentage of dissolved inorganic carbon from water taken up by the plants (DIC  $^{14}\text{C}$  [%]) is based on the relative difference between the  $F^{14}\text{C}_{\text{atm}}$  value (see above) and the  $F^{14}\text{C}$  value in the plant ( $F^{14}\text{C}_{\text{plant}}$ ) as well as the water ( $F^{14}\text{C}_{\text{water (modeled)}}$ ):

$$\text{DIC } ^{14}\text{C} (\%) = \left(\frac{F^{14}\text{C}_{\text{atm}} - F^{14}\text{C}_{\text{plant}}}{F^{14}\text{C}_{\text{atm}} - F^{14}\text{C}_{\text{water (modeled)}}}\right) * 100 \quad (4)$$

$F^{14}\text{C}_{\text{water (modeled)}}$  is calculated according to Eq. (5). The treated plants had two different water sources, namely spray water (ca. 1.64 vol%) and irrigation water (ca. 98.36 vol%; see section 2.1) with measured  $F^{14}\text{C}_{\text{spray water}}$  and  $F^{14}\text{C}_{\text{irrigation water}}$  concentration. DIC potentially taken up by the plants via their roots (mainly) originates from irrigation water. All treatment groups were irrigated with the same irrigation water (G-GW) as well as with the same amount of irrigation water. Accordingly, isotope differences between treatment groups are not caused by irrigation water. Nevertheless, irrigation water is a relevant source of DIC for all plants and has to be considered:

$$F^{14}\text{C}_{\text{water (modeled)}} = \frac{\% \text{ spray water}}{100} * F^{14}\text{C}_{\text{spray water}} + \frac{\% \text{ irrigation water}}{100} * F^{14}\text{C}_{\text{irrigation water}} \quad (5)$$

The DIC concentration of the modeled water is a mixture of the concentration found in the spray and irrigation water, calculated as

$$[\text{DIC}]_{\text{water (modeled)}} = \% \text{ spray water} * [\text{DIC}]_{\text{spray water}} + \% \text{ irrigation water} * [\text{DIC}]_{\text{irrigation water}} \quad (6)$$

Potential differences in the DIC concentration of the different water sources (spray water, irrigation water) are reflected by  $F^{14}\text{C}_{\text{water (modeled)}}$  due to the existing relationship between the radiocarbon concentration and the DIC concentration in water (see, e.g., Wang et al. 2022).

Plants discriminate against  $^{13}\text{C}$  or  $^{14}\text{C}$  in their carbon source (e.g., atmospheric  $\text{CO}_2$ ). Discrimination against  $^{13}\text{C}$  ( $\Delta^{13}\text{C}$ ) or  $^{14}\text{C}$  ( $\Delta^{14}\text{C}$ ) can be calculated based on the following formula:

$$\Delta = \frac{\frac{\delta_{\text{source}}}{1000} - \frac{\delta_{\text{plant}}}{1000}}{1 + \frac{\delta_{\text{plant}}}{1000}} * 1000 \text{ (after Farquhar et al. 1989)} \quad (7)$$

In contrast to  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ ,  $\Delta^{13}\text{C}$  and  $\Delta\Delta^{14}\text{C}$  allow investigation into biological processes (Farquhar and Lloyd 1993). For discrimination against  $^{13}\text{C}$  and  $^{14}\text{C}$  of atmospheric  $\text{CO}_2$ ,  $\delta_{\text{source}}$  was set to  $\delta^{13}\text{C}_{\text{atm}} = -8.5\text{‰}$  (Cernusak and Ubierna 2022) and  $\Delta^{14}\text{C}_{\text{atm}} = -3.6560\text{‰}$  (group 1) or  $\Delta^{14}\text{C}_{\text{atm}} = -4.0200\text{‰}$  (group 2; see above), respectively. For  $\delta_{\text{plant}}$ , the measured IRMS  $\delta^{13}\text{C}_{\text{cellulose}}$  values (see also Göhring et al. 2023a) were used and the age-corrected  $\Delta^{14}\text{C}_{\text{plant}}$  values were calculated according to

$$\Delta^{14}\text{C} = (F^{14}\text{C} * e^{\lambda_c(1950-x)} - 1) * 1000 \text{ (Stenström et al. 2011)} \quad (8)$$

with  $\lambda_c = \frac{\ln(2)}{5730 \text{ a}}$  and  $x = 2020$  (year of growth/sampling). The discrimination of plants against  $^{13}\text{C}$  and  $^{14}\text{C}$  of DIC in spray water is based on the  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  values measured for the spray water samples and can be calculated according to Eq. (6) (with source = DIC).

The control plants (G-0/G-4) grew in the same chamber and, thus, under the same atmosphere, as the different treatment groups. They were also irrigated with the same tap water as all other groups. Accordingly, deviations in the isotopic composition of the plants of the different treatment groups from the isotopic signature observed for the corresponding control groups is an indicator for sea spray related effects.

### 3. Results

Our main objective was to study possible effects in the  $^{14}\text{C}$  composition of plants which were sprayed during growth with water containing different amounts of minerals, including DIC, and salt (NaCl), and thereby mimicking effects of sea spray.

The radiocarbon composition of the water used for the experiments is presented in Table 2. All plants were irrigated with tap water G-GW with a radiocarbon concentration of  $F^{14}\text{C} 0.9337 \pm 0.0031$ , indicating the admixture of a few percent of fossil carbon within the aquifer. The tap spray water used for the control samples G-0 (group 1) and G-4 (group 2), was identical. This water contained a radiocarbon concentration of  $F^{14}\text{C} 0.9191 \pm 0.0029$  and thus contained a bit more fossil carbon than the irrigation water. The mineral salt mixed to the spray water solutions of G-3 (“brackish-like”) and G-1 (“marine-like”) apparently contained a higher amount of fossil carbon compared to the control samples since the resulting spray water show a  $F^{14}\text{C}$  of about  $0.9006 \pm 0.0030$  and  $0.8707 \pm 0.0030$ , respectively. Unfortunately, the radiocarbon measurements of the spray water of G-2 (“>>marine”) failed due to a broken sample container. The salty spray water of G-5 (“Schlei”) and G-6 (“Baltic”) were more enriched in  $^{14}\text{C}$  (G-5:  $0.9437 \pm 0.0030$ ; G-6:  $0.9638 \pm 0.0031$ ) compared to the spray water of G-0/G-4, G-3, and G-1.

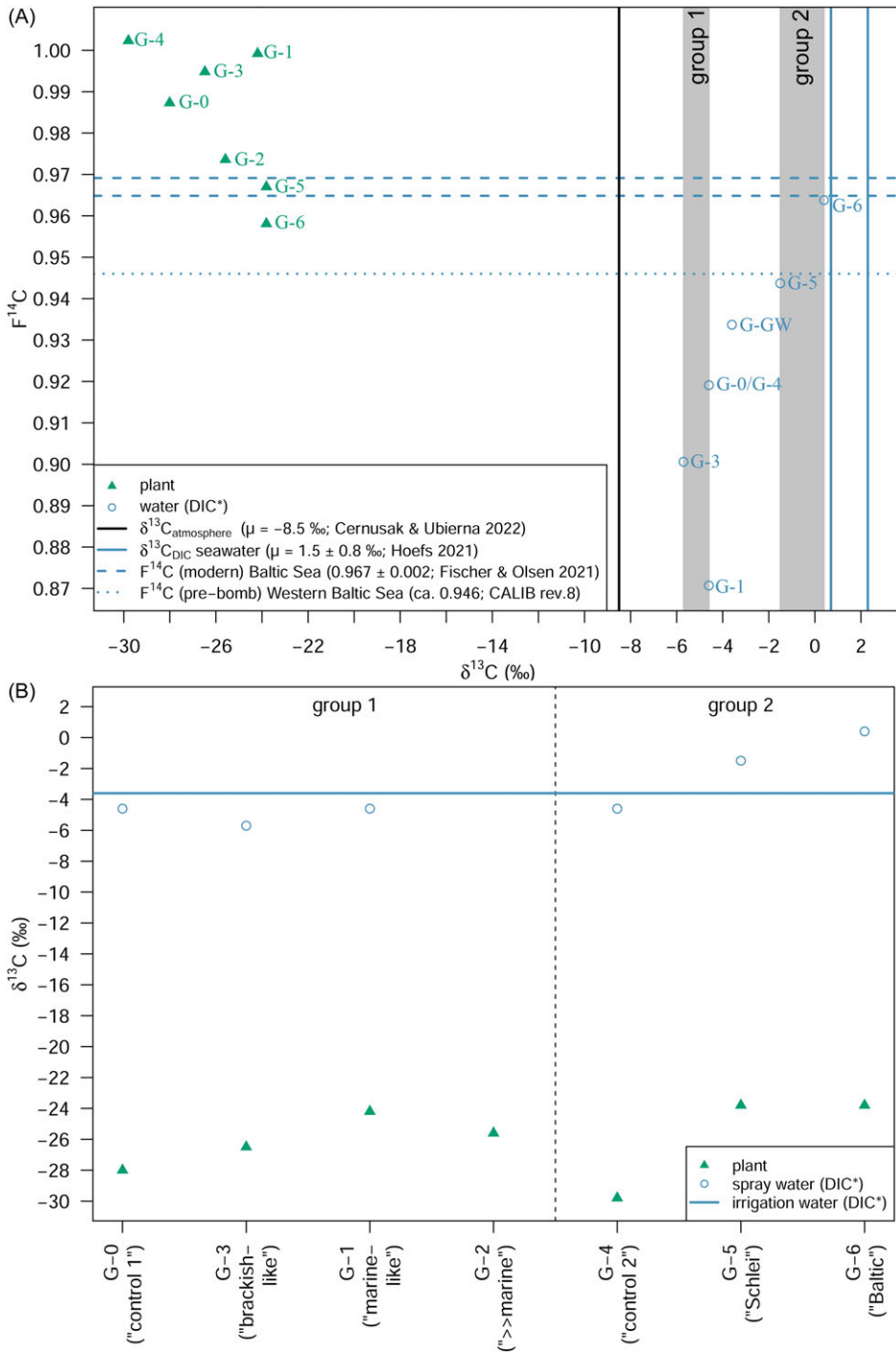
The irrigation water G-GW and the spray water of the control treatments G-0 (“control 1”) and G-4 (“control 2”) contained 162.5 mg/L and 298.4 mg/L dissolved inorganic carbon (DIC), measured as mg  $\text{CO}_2$ , respectively. Spray water used for the treatments G-3 and G-1 contained a slightly higher DIC content (309.1 mg/L and 331.7 mg/L, respectively). The natural salty water from the Schlei inlet (G-5) and the Baltic Sea (G-6) contained markedly lower DIC concentrations of 125.6 mg/L and 79.6 mg/L, respectively (see Figure S1 and Table 1).

The results for the radiocarbon analyses on the plant samples are presented in Table 2 and visualized in Figure 3A. Estimated radiocarbon concentration for plants of the treatments G-0 (“control 1”), G-3 (“brackish-like”), and G-1 (“marine-like”) give  $^{14}\text{C}$  signatures which are depleted with respect to atmospheric  $^{14}\text{C}$ . The plant sample of treatment G-4 (“control 2”) exhibit, as expected, a radiocarbon concentration close to average atmospheric  $^{14}\text{C}$  over the growth period. The experimental conditions of treatments G-0 and G-4 differ in the growth period of both treatments (G-0: June–December; G-4: July–December), while the composition of used irrigation and spray water are the same. The depleted radiocarbon content of G-0 plant tissue with a magnitude comparable to treatments G-1 and G-3 seem to



**Table 2.**  $^{14}\text{C}$  age,  $F^{14}\text{C}$  ( $\pm$  standard deviation  $\sigma$ ), and  $\Delta^{14}\text{C}$  (see Eq. 7) for plant leaves, spray water, and irrigation water samples from the greenhouse as well as modeled  $F^{14}\text{C}$  and corresponding  $\Delta^{14}\text{C}$  (see Eq. 7) in water ( $F^{14}\text{C}_{\text{modeled}}$ ; see Eq. 5), calculated percentage of fossil  $^{14}\text{C}$  in plants (fossil  $^{14}\text{C}$  (%); see Eq. 3), and calculated percentage of  $^{14}\text{C}$  in plants originating from dissolved inorganic carbon (DIC) in (spray or irrigation) water (DIC  $^{14}\text{C}$  (%); see Eq. 4). NA = not available

	G-0	G-3	G-1	G-2	G-4	G-5	G-6
	“control 1”	“brackish-like”	“marine-like”	“>>marine”	“control 2”	“Schlei”	“Baltic”
Plant lab ID	KIA-56811	KIA-56814	KIA-56812	KIA-56813	KIA-56815	KIA-56816	KIA-56817
Plant $^{14}\text{C}$ age	modern	modern	modern	215 $\pm$ 23 BP	modern	269 $\pm$ 22 BP	344 $\pm$ 23 BP
Plant $F^{14}\text{C}$	0.9873 $\pm$ 0.0028	0.9948 $\pm$ 0.0026	0.9992 $\pm$ 0.0027	0.9736 $\pm$ 0.0027	1.0023 $\pm$ 0.0028	0.9670 $\pm$ 0.0026	0.9581 $\pm$ 0.0027
Plant $\Delta^{14}\text{C}$	-21.02	-13.59	-9.23	-34.61	-6.15	-41.15	-49.98
Spray water lab ID	KIA-56819	KIA-56822	KIA-56820	KIA-56821	KIA-56819	KIA-56823	KIA-56924
Spray water $^{14}\text{C}$ age	678 $\pm$ 26 BP	841 $\pm$ 27 BP	1113 $\pm$ 28 BP	NA	678 $\pm$ 26 BP	465 $\pm$ 26 BP	296 $\pm$ 26 BP
Spray water $F^{14}\text{C}$	0.9191 $\pm$ 0.0029	0.9006 $\pm$ 0.0030	0.8707 $\pm$ 0.0030	NA	0.9191 $\pm$ 0.0029	0.9437 $\pm$ 0.0030	0.9638 $\pm$ 0.0031
Spray water $\Delta^{14}\text{C}$	-88.65	-106.99	-136.64	NA	-88.65	-64.26	-44.33
Irrigation water lab ID				KIA-56818			
Irrigation water $F^{14}\text{C}$				0.9337 $\pm$ 0.0031 (all groups)			
Irrigation water $\Delta^{14}\text{C}$				-74.17 (all groups)			
Water $F^{14}\text{C}$ (modeled)	0.9335	0.9332	0.9327	0.9184	0.9335	0.9339	0.9342
Water $\Delta^{14}\text{C}$ (modeled)	-74.41	-74.71	-75.20	NA	-74.41	-74.01	-73.68
Fossil $^{14}\text{C}$ (%) in plants	1.74	1.00	0.56	3.11	0.21	3.73	4.61
DIC $^{14}\text{C}$ (%) in plants	24.32	13.69	7.48	NA	3.00	53.40	67.30



**Figure 3.** (A)  $F^{14}C$  plotted against  $\delta^{13}C$  for beach grass leaves ( $\alpha$ -cellulose; washed), spray water (dissolved inorganic carbon (DIC)), and irrigation water (G-GW; DIC) for group 1 (mineral salt solution; control G-0 (“control 1”), G-3 (“brackish-like”), G-1 (“marine-like”), G-2 (“>>marine”)) and group 2 (control G-4 (“control 2”), Schlei water next to Haithabu (G-5, “Schlei”) and Baltic Sea water next to Fehmarn (G-6, “Baltic”)), respectively. (B)  $\delta^{13}C$  data for  $\alpha$ -cellulose and bulk in beach grass leaves (washed) as well as for dissolved inorganic carbon (DIC) in spray water and irrigation water for group 1 and group 2 (see above; modified after Göhring et al. 2023a). \* =  $\delta^{13}C_{DIC}$  values were measured via AMS (could contain fractionation effects from ionization) and are given only for indicating the magnitude in  $^{13}C$  composition (see indicated ranges (grey) in (A)); see Tables 2 and S1.

indicate a larger influence of the fossil carbon containing irrigation and spray waters, as compared with treatment G-4 and need further verification.

In contrast to the above mentioned treatments, plants of treatments G-2 (“>>marine”), G-5 (“Schlei”), and G-6 (“Baltic”) give distinctly more depleted  $^{14}\text{C}$  concentrations of  $0.9736 \pm 0.0027$ ,  $0.9670 \pm 0.0026$ , and  $0.9581 \pm 0.0027$ , respectively (see Figure 3A and Table 2).

The plant tissue of treatments G-5 and G-6 exhibit radiocarbon concentrations close to the corresponding spray water samples in the range expected for modern Baltic Sea water (i.e.,  $F^{14}\text{C}$   $0.967 \pm 0.002$ ; Fischer and Olsen 2021) in case of G-6 (“Baltic”) and rather close to the (pre-bomb) Western Baltic seawater value (ca.  $F^{14}\text{C}$  0.946; CALIB rev. 8, Stuiver and Reimer 1993; Heaton et al. 2020) in case of G-5 (“Schlei”; see Figure 3A, Table 2). While we cannot say anything about the isotopic signature of the spray water used for treatment G-2 (see above), the measured  $^{14}\text{C}$  concentration of the corresponding plant sample is comparable to the concentration measured in plant tissues of treatments G-5 and G-6, and again close to the range for Baltic Sea water, although these plants were not sprayed with natural brackish water (see section 2.1).

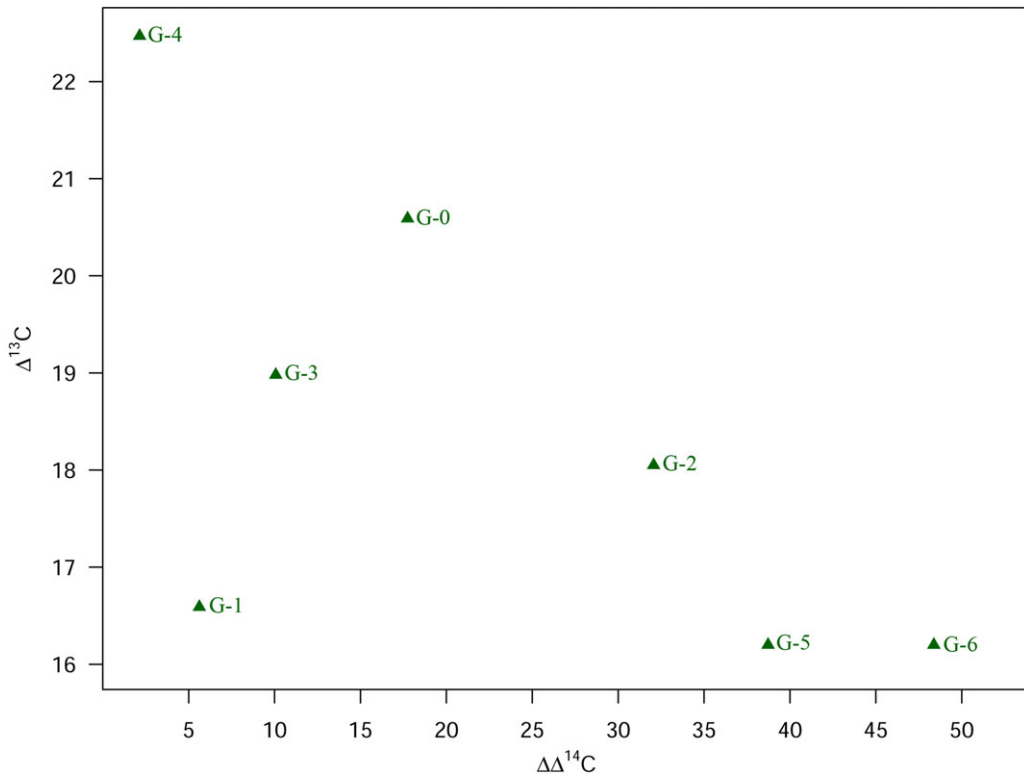
Assuming atmospheric  $\text{CO}_2$  was the major carbon source for the plants, we calculated the discrimination of the plants of the different treatment groups against atmospheric  $^{13}\text{C}$  ( $\Delta^{13}\text{C}$ ) and  $^{14}\text{C}$  ( $\Delta\Delta^{14}\text{C}$ ) (see Eq. 6), respectively (see Table 3). The discrimination against atmospheric  $^{13}\text{C}$  as well as  $^{14}\text{C}$  decreases in plants of group 1 (non-salty) treatments G-3 (“brackish-like”) and G-1 (“marine-like”) compared to the corresponding control plants of G-0 (see Figure 4, Table 3). With an increasing mineral concentration in the spray water ( $\text{G-0} < \text{G-3} < \text{G-1}$ ; see Table 1), the discrimination in  $^{14}\text{C}$  becomes smaller as compared to the discrimination against  $^{13}\text{C}$  (Figures S2 and S3) resulting in a lowering of the calculated  $\Delta\Delta^{14}\text{C}/\Delta^{13}\text{C}$  ratio (Table 3). Plants of treatment G-2 (“>>marine”) show a discrimination against  $^{13}\text{C}$  of comparable magnitude as seen for G-1 and G-3. However, with respect to  $^{14}\text{C}$  the discrimination is about 2-times higher than the discrimination against  $^{13}\text{C}$ , comparable to group 2 treatments (Figures S2–S4, Table 3). For the group 2 plants of treatments G-4 (“control 2”), G-5 (“Schlei”), and G-6 (“Baltic”) the discrimination against atmospheric  $^{13}\text{C}$  decreases with increasing salinity (psu; see Table 1). In contrast, discrimination against  $^{14}\text{C}$  strongly increases in G-5 and G-6 plants compared to that found for the control treatment G-4 or the group 1 treatments. The isotopic discrimination against atmospheric  $^{13}\text{C}$  is, however, of comparable magnitude as seen in group 1 treatments of G-3 and G-1 (Figures S2A and S3A). Assuming a major carbon uptake via the atmosphere and a fossil  $^{14}\text{C}$  concentration of 0  $F^{14}\text{C}$ , the proportion of atmospheric fossil carbon in the plants can be calculated (see Eq. 3). The estimated fossil carbon contribution is low, is up to about 3% (G-2) in group 1 and up to about 5% (G-6) in group 2 (Figure 5, Table 2).

The above discussed carbon isotope discrimination factors were calculated relative to atmospheric  $\text{CO}_2$  as the sole carbon source for the plants and, thus, ignoring carbon derived from water, i.e. DIC. A comparable estimation against water  $\text{DI}^{13}\text{C}$  isotopic composition, i.e.  $\Delta^{13}\text{C}_{\text{DIC}}$ , is hampered by the fact that water  $\delta^{13}\text{C}_{\text{DIC}}$  was only measured by AMS and not by conventional IRMS, thus also contain effects caused by the ionization process. Uncertainties in the analysis as well as accuracies are worse and measurements might deviate from conventional IRMS analyses by about 1.5–2%. Nevertheless, a brief comparison of the discrimination effects relative to spray water DIC is given (see Table 3).

If the carbon uptake in the plant tissue during the growth experiment did not only occur via atmospheric  $\text{CO}_2$  but also (via the water path (irrigation and spray water), the proportion of  $^{14}\text{C}$  from DIC can be calculated. According to Eq. (4), plants of G-5 (“Schlei”) and G-6 (“Baltic”) received about 53% and 67% of the carbon from DIC. The percentage of  $^{14}\text{C}$  originating from DIC is lower for plants of group 1 with values between 7% (G-1) and 24% (G-0) (Figure 5). Unfortunately, no water DIC proportion could be calculated for G-2 (for reasons given above). As visible from Figure S4, the percentage of  $^{14}\text{C}$  taken up from DIC by group 2 plants G-5 and G-6 increases with increasing salinity levels, compared to their control group G-4. We observe an opposite such trend for plants of group 1, with (slightly) increasing DIC,  $[\text{Na}^+]$ , and  $[\text{Cl}^-]$  levels ( $\text{G-0} < \text{G-3} < \text{G-1}$ ; see Figures S2, S4–S6). Figure 3B illustrates that the  $\delta^{13}\text{C}_{\text{cellulose}}$  values of the plants are not only influenced by the  $\delta^{13}\text{C}_{\text{DIC}}$  value of the irrigation water (−3.6‰; Figure 3B, Table S1) or of atmospheric  $\text{CO}_2$  (ca. −8.5‰; Cernusak

**Table 3.** Discrimination against  $^{13}\text{C}$  ( $\Delta^{13}\text{C}$ ) and  $^{14}\text{C}$  ( $\Delta\Delta^{14}\text{C}$ ) as well as calculated relative ratio of discrimination against  $^{13}\text{C}$  and  $^{14}\text{C}$  ( $\Delta\Delta^{14}\text{C}/\Delta^{13}\text{C}$ ) assuming atmospheric  $\text{CO}_2$  or DIC in spray water or modeled water as the only carbon source for the investigated plants. NA = not available

Sample ID	Label	C source = atmospheric $\text{CO}_2$ only			C source = DIC only				
		$\Delta^{13}\text{C}$	$\Delta\Delta^{14}\text{C}$	$\Delta\Delta^{14}\text{C}/\Delta^{13}\text{C}$	$\Delta^{13}\text{C}$	$\Delta\Delta^{14}\text{C}_{\text{spray water}}$	$\Delta\Delta^{14}\text{C}/\Delta^{13}\text{C}$	$\Delta\Delta^{14}\text{C}_{\text{modeled water}}$	$\Delta\Delta^{14}\text{C}/\Delta^{13}\text{C}$
G-0	“control 1”	20.59	17.74	0.86	24.08	-65.40	-2.72	-51.45	-2.14
G-3	“brackish-like”	18.98	10.07	0.53	21.35	-90.48	-4.24	-59.02	-2.76
G-1	“marine-like”	16.59	5.62	0.34	20.08	-123.00	-6.13	-63.52	-3.16
G-2	“>>marine”	18.05	32.06	1.78	NA	NA	NA	NA	NA
G-4	“control 2”	22.47	2.14	0.10	25.97	-79.33	-3.05	-65.58	-2.52
G-5	“Schlei”	16.20	38.73	2.39	22.85	-21.08	-0.92	-30.78	-1.35
G-6	“Baltic”	16.20	48.38	2.99	24.80	7.87	0.32	-21.44	-0.86

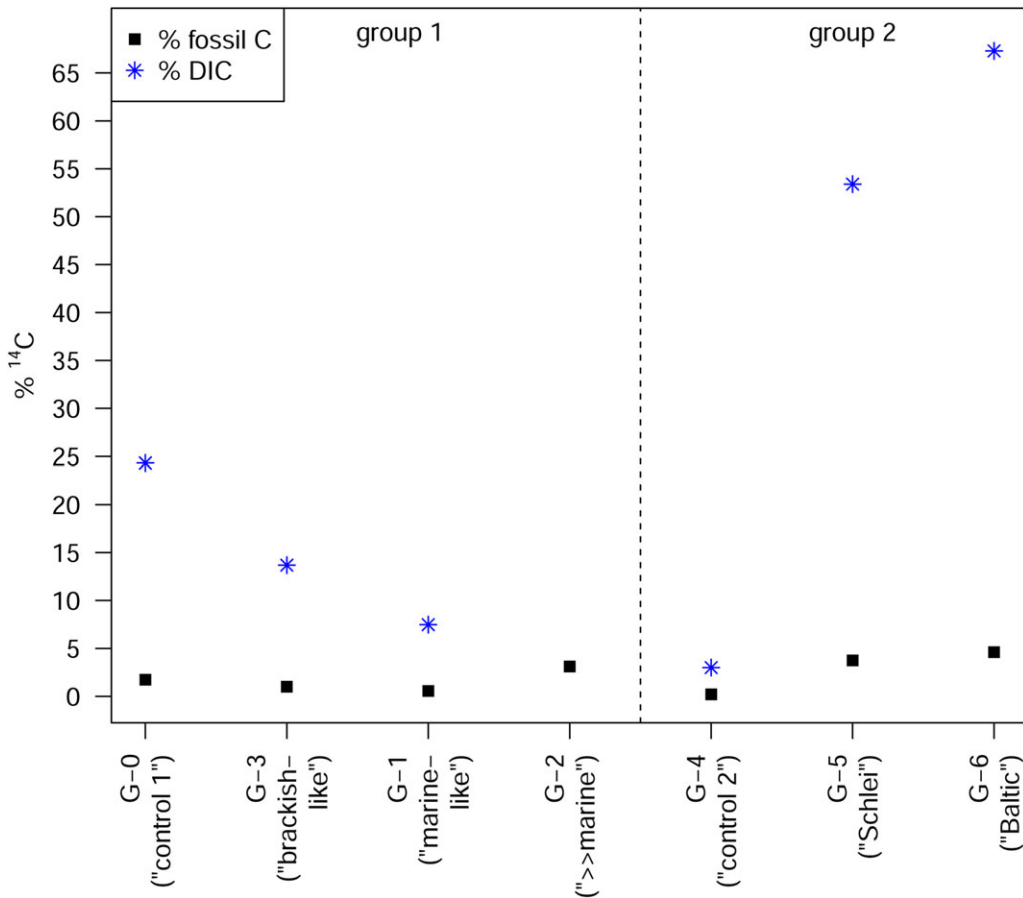


**Figure 4.** Discrimination against  $^{13}\text{C}$  ( $\Delta^{13}\text{C}$ ) versus discrimination against  $^{14}\text{C}$  ( $\Delta\Delta^{14}\text{C}$ ) in atmospheric  $\text{CO}_2$  (filled symbols) for group 1 (mineral salt solution; control G-0 (“control 1”), G-3 (“brackish-like”), G-1 (“marine-like”), G-2 (“ $\gg$ marine”)) and group 2 (control G-4 (“control 2”), Schlei water next to Haithabu (G-5, “Schlei”) and Baltic Sea water next to Fehmarn (G-6, “Baltic”)), respectively (see Table 3).

and Ubierna 2022). With  $\delta^{13}\text{C}_{\text{DIC}}$  values of about  $-1.5\text{‰}$  (G-5, “Schlei”) and  $0.4\text{‰}$  (G-6, “Baltic”) the spray water samples are as expected for Baltic Sea water (brackish water) and seawater ( $\delta^{13}\text{C}_{\text{DIC}} \approx 1.5\text{‰} \pm 0.8\text{‰}$ ) in general (Hoefs 2021; Kroopnick et al. 1972; Kroopnick 1985).

The sea spray effect on the stable and radiogenic isotopic signature of the sprayed plants can also be visualized for  $\delta^{34}\text{S}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  (Figures S7B and S8B, Table S1): Plants of treatments G-5 and G-6 are shifted towards seawater values with  $\delta^{34}\text{S} \approx 20\text{--}21\text{‰}$  and  $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7092$ , respectively (Andersson et al. 1992; Rees et al. 1978; Tostevin et al. 2014). While plants of G-3 are enriched in  $^{34}\text{S}$  compared to control G-0 and while plants of G-1 are enriched in  $^{34}\text{S}$  compared to G-3, depletion in  $^{34}\text{S}$  is observable for G-2 (Figure S7B, Table S1). With respect to  $^{87}\text{Sr}/^{86}\text{Sr}$ , plants of group 1 are shifted towards lower values, i.e. towards the isotope ratio of their corresponding spray water, with increasing Sr concentration. G-2 plants, sprayed with water exhibiting the highest Sr concentration within group 1, are shifted the most (Figure S8B, Table S1; see also Göhring et al. 2023a).

We, thus, have to distinguish two different models of behavior in both the stable isotope fingerprints as well as the radiocarbon signature ( $\text{F}^{14}\text{C}$ ,  $\Delta^{14}\text{C}$ ) as a result of the artificial sea spray treatment: a shift towards a seemingly marine stable isotope as well as radiocarbon signature (G-5, G-6) in the (salty) group 2 and a shift towards a seemingly marine radiocarbon signature, but divergent stable isotope data (G-2; (mineral salt solution) group 1), resulting from different mechanisms (see section 4.1).



**Figure 5.** Calculated proportion of fossil (atmospheric)  $^{14}\text{C}$  as well as proportion of  $^{14}\text{C}$  from water (DIC) taken up by the greenhouse plants of group 1 (mineral salt solution; control G-0 ("control 1"), G-3 ("brackish-like"), G-1 ("marine-like"), G-2 (">>marine")) and group 2 (control G-4 ("control 2"), Schlei water next to Haithabu (G-5, "Schlei") and Baltic Sea water next to Fehmarn (G-6, "Baltic")), respectively; see also Table 2.

## 4. Discussion

### 4.1 Sea spray effect, salinity stress, $\text{HCO}_3^-$ stress, and $^{14}\text{C}$ analysis of plant samples

Our study demonstrates the impact of sea spray on radiocarbon analyses of terrestrial plants. In principle, two types of spray water have been used, i.e. (i) mineral salt solution, originating from tap water, containing increasing ion concentrations (e.g., DIC,  $\text{Na}^+/\text{Cl}^-$ ), and slightly higher radiocarbon concentrations (group 1; G-1 to G-3; control G-0), and (ii) salty water (higher NaCl concentration), originating from marine sources (group 2; G-5 and G-6; control G-4).

With increasing ion concentration within the (non-salty) spray water of group 1, the radiocarbon content in the water decreases (G-0:  $0.9191 \pm 0.0029$ , G-3:  $0.9006 \pm 0.0030$ ; G-1:  $0.8707 \pm 0.0029$ ; see Figure 3A), probably the result of differences in the DIC content (see also Figure S1). This is in accordance with the findings of Wang et al. (2022) who found a linear relationship between  $^{14}\text{C}$  concentration and  $1/[\text{DIC}]$ . For spray waters of group 2 with larger NaCl concentrations we observe higher  $^{14}\text{C}$  concentrations compared to the tap water (see Table 2).

Soil respiration is known to be a potential source of atmospheric  $\text{CO}_2$ , originating from soil carbon. Soil respiration is mainly driven by three biological processes, namely microbial respiration, root

respiration, and faunal respiration and soil manuring has a high impact on soil respiration. While microorganisms might have been naturally present in the soil used for the experiment, no larger organisms (e.g. earthworm) were present in the soil. Thus, we can exclude faunal respiration. The soil was not manured during the experiments. Thus, manuring effects on the soil can also be excluded. Sandy soils, as used for this experiment (see section 2.1), typically have a low SOM (soil organic matter) and SOC (soil organic carbon) content and low available water capacity. This limits soil respiration and mineralization of nitrogen. Therefore, sandy soils show a very low soil respiration activity. In ecosystems where the soil CO<sub>2</sub> production is very low due to low biological activity, CO<sub>2</sub> consumptive processes (dissolution in water, biological activities, chemical reactions) in the soil are higher than CO<sub>2</sub> production processes (e.g. Sánchez-Cañete et al. 2018). The impact of SOC and DIC as source of atmospheric CO<sub>2</sub> via respiration processes can be neglected in our study. In addition, any minor impact would have affected the atmosphere of all treatment groups, growing under the same atmosphere in the climate chamber, including the control groups. The radiocarbon content of the plants is known due to the experimental design and should reflect the atmospheric <sup>14</sup>C concentration during the growth period, i.e. they should exhibit a modern <sup>14</sup>C signature (group 1, June–December 2020: F<sup>14</sup>C<sub>atm</sub> = 1.0048, group 2, July–December 2020: F<sup>14</sup>C<sub>atm</sub> = 1.0044). The atmospheric <sup>14</sup>C concentration should only be understood as an approximation for the climate chamber's atmosphere, reflecting the HPB atmosphere during the growth period. F<sup>14</sup>C values close to the HPB atmospheric F<sup>14</sup>C values are observed for treatment G-4 (“control 2”; 1.0023 ± 0.0028). In contrast, plants of the control treatment G-0 (0.9873 ± 0.0028) exhibit an unexpected low <sup>14</sup>C concentration, compared to the contemporary atmospheric concentration. Differences between control plants of G-0 and G-4 are also observable to some extent with respect to δ<sup>13</sup>C<sub>cellulose</sub> (G-0: −28.01‰, G-4: −29.80‰), δ<sup>34</sup>S<sub>total S</sub> (G-0: 5.50‰, G-4: 5.96‰), and <sup>87</sup>Sr/<sup>86</sup>Sr (G-0: 0.709340, G-4: 0.708845) (see Table S1). The corresponding δ<sup>18</sup>O<sub>cellulose</sub> values, however, do not differ (G-0: 30.98‰, G-4: 31.01‰; see Göhring et al. 2023a for details).

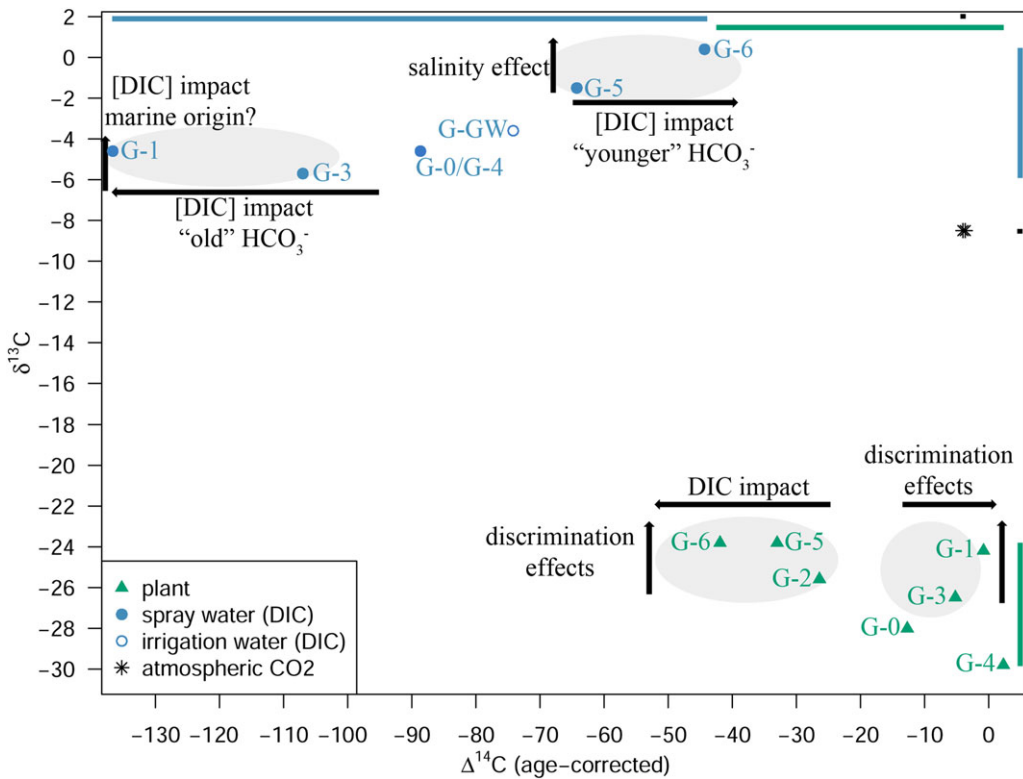
The control groups grew in the same greenhouse chamber, thus under the same atmosphere, and were treated identically to each other (sprayed with identical spray water, irrigated with identical tap water). The group 1 experiment started in June 2020, while the group 2 experiment started in July 2020. These differences (also with respect to atmosphere) should be minor; however, a potential effect of the different starting point (and run time) cannot fully be excluded. Another difference potentially affecting the radiocarbon concentration in the G-0 and G-4 plants could result from the fact that two different seed batches, delivered in two different packages, were used when growing the plants of group 1 and 2, respectively. In addition, a new bag of lawn soil and lawn sand has to be used to set up the soil for group 2. We cannot fully exclude differences in potentially different stocks of seeds or soil/sand. Preliminary isotope analyses on seed, plant, and soil samples (δ<sup>13</sup>C<sub>cellulose</sub>, δ<sup>18</sup>O<sub>cellulose</sub>, δ<sup>34</sup>S<sub>total S</sub>, <sup>87</sup>Sr/<sup>86</sup>Sr), however, point to inter-individual differences rather than batch differences (see Göhring et al. 2023a).

Accordingly, differences in the control plants of G-0 and G-4 with respect to F<sup>14</sup>C as well as stable isotope values might partly be due to differences within the growth period, with a shorter growth period (G-0: June–December; G-4: July–December), with some additional influences of potential inter- (or also intra-) plant variation (see Göhring et al. 2023a for intra-leaf variation in δ<sup>13</sup>C<sub>cellulose</sub> and δ<sup>18</sup>O<sub>cellulose</sub>). Further analyses, including multiple isotopic measurements of samples of the same treatment groups, are required to investigate the observed differences.

The treatments G-1 (“marine-like”) and G-3 (“brackish-like”) also exhibit radiocarbon concentrations slightly lower than the (expected) atmospheric value, indicating some impact of DIC via spray or irrigation water, or both.

Figure 6 shows that the δ<sup>13</sup>C and Δ<sup>14</sup>C signatures of the investigated plant treatment groups are influenced in different ways. We can differentiate between several influencing factors that affect the δ<sup>13</sup>C or the Δ<sup>14</sup>C signature of the plants. The processes involved are explained in the following:

Figures S5 and S6 illustrate decreased discrimination against both <sup>13</sup>C and <sup>14</sup>C with increasing levels of, e.g., Na<sup>+</sup> or Cl<sup>-</sup>, when considering plants of the G-0 (“control 1”), G-3 (“brackish-like”), and G-1 (“marine-like”) treatment groups. The DIC concentration (i.e., HCO<sub>3</sub><sup>-</sup>) apparently has a similar effect on the isotopic composition of plants of treatment groups G-3 and G-1 (Figures S1–S4, see also Table 3).



**Figure 6.**  $\delta^{13}\text{C}$  values for plants, atmospheric  $\text{CO}_2$  and spray water (DIC) as well as irrigation water (DIC; G-GW) plotted against the corresponding age-corrected  $\Delta^{14}\text{C}$  values for the different treatment groups (see Tables 2 and S1): group 1 (mineral salt solution; control G-0 (“control 1”), G-3 (“brackish-like”), G-1 (“marine-like”), G-2 (“>>marine”)) and group 2 (control G-4 (“control 2”), Schlei water next to Haihabu (G-5, “Schlei”) and Baltic Sea water next to Fehmarn (G-6, “Baltic”). The arrows indicate major effects on the isotope values (see text). The bars on the edges serve for an illustration of the range of the  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  values in plant (green), spray water (blue), atmosphere (black). [color online].

As shown by Tavakkoli et al. (2011; 2010) stomatal conductance decreases with increasing levels of both  $\text{Na}^+$  and  $\text{Cl}^-$ . While the  $\text{Na}^+$  levels are comparably low in the irrigation water (G-GW; 9.70 mg/L) as well as the spray water of G-3 (37.82 mg/L) and G-1 (75.63 mg/L), respectively, both spray water sources contain already rather high levels of  $\text{Cl}^-$  (G-3: 558.65 mg/L; G-1: 1117.30 mg/L). Far lower  $\text{Cl}^-$  levels can already have a distinct impact on stomatal conductance,  $\text{CO}_2$  assimilation rate, or on the ratio of intracellular versus atmospheric  $\text{CO}_2$  concentration ( $c_i/c_a$ ) (Tavakkoli et al. 2011; 2010). The DIC concentration in spray water used for treatments G-0/G-4, G-3, and G-1 varies between 298.4 mg/L (G-0/G-4) and 331.7 mg/L (G-1) which is distinctly more than the amount measured in the natural salty waters of the Schlei inlet (G-5, 125.6 mg/L) and the Baltic Sea (G-6, 79.6 mg/L; see Table 1). A higher amount of DIC available to the plants should elevate partial intercellular  $\text{CO}_2$  pressure ( $p_i$ ) via carbonic anhydrase reactions ( $\text{HCO}_3^- \rightarrow \text{CO}_2$ ), resulting in an increased discrimination against  $^{13}\text{C}$  as well as  $^{14}\text{C}$ . Accordingly, for group 1 treatments, increasing  $\text{Cl}^-$  as well as elevated DIC concentrations could cause a reduced stomatal conductance, resulting in decreased isotopic discrimination, as documented in Table 3 and Figure 6 (see also Figures S2 and S6).

Plants of treatments G-5 (“Schlei”) and G-6 (“Baltic”) give  $^{14}\text{C}$  concentrations of  $F^{14}\text{C}$  0.9670 ( $\pm 0.0026$ ) and  $F^{14}\text{C}$  0.9581 ( $\pm 0.0027$ ), respectively. In addition, also plants of treatment G-2 (“>>marine”) show a low  $^{14}\text{C}$  concentration ( $0.9736 \pm 0.0027$ ; Figure 3A, Table 2). Plants of G-5



(“Schlei”) and G-6 (“Baltic”) grew under salinity stress as spray water of both treatment groups contained quite high  $\text{Na}^+$  and  $\text{Cl}^-$  levels (see Table 1). These concentrations are markedly higher than that found for the other spray water of group 1 as well as higher than those in tap water used as spray water source or for irrigating the plants of all treatment groups.

On a physiological level, salinity causes reduced stomatal conductance in plants (Brugnoli and Lauteri 1991; Poschenrieder et al. 2018; Seemann and Critchley 1985), which in turn has an effect on e.g.,  $\delta^{13}\text{C}_{\text{cellulose}}$  in plants, expressed by enrichment in  $^{13}\text{C}$  (Figure 3B, Table 3) (Göhring et al. 2023a; Göhring et al. 2023b; Roden et al. 2005; Zhang et al. 2019). Low stomatal conductance causes a decrease in the intercellular partial pressure of  $\text{CO}_2$  ( $p_i$ ) and, thus, a reduced intercellular  $\text{CO}_2$  concentration ( $c_i$ ) (Seemann and Critchley 1985; Winter 1981). Under salt stress, the ratio of intercellular and atmospheric  $\text{CO}_2$  concentration ( $c_i/c_a$ ) is reduced (Farquhar et al. 1982). Accordingly, discrimination against  $^{13}\text{C}$  decreases with increasing salinity levels as seen in  $\Delta^{13}\text{C}$  of treatment groups G-4 and G-5/G-6 (see Figures 6 and S3A, Table 3). We would expect similar and even more pronounced effects for  $\Delta\Delta^{14}\text{C}$ , but instead plants of treatments G-5 and G-6 show a  $\Delta\Delta^{14}\text{C}$  of about 38‰ and 48‰, respectively, distinctly larger than in plants of control G-4 (6.6‰) or group 1 treatments G-1 and G-3 (Figure 6, Table 3). Apparently, some carbon, depleted in  $^{14}\text{C}$  relative to atmospheric carbon, still enter the plant as  $\text{H}^{14}\text{CO}_3^-$  via the roots. The proportion of  $^{14}\text{C}$  originating from DIC within both spray water and irrigation water (%DIC) in the plants increases in treatment G-5 (ca. 53%) and G-6 (ca. 67%) compared to the corresponding control plants of G-4 (“control 2”; ca. 3%; see Figures 5 and S4, Table 2). Although atmospheric  $\text{CO}_2$  uptake is reduced due to stomatal closure, the high amount of available DIC (i.e.,  $\text{HCO}_3^-$ ) in the brackish water (G-5, G-6) – compared to the amount of DIC available to the control plants G-4 – results in an increased discrimination against  $^{14}\text{C}$  (see also Figure 6), which is even more pronounced than the reverse effect of reduced stomatal conductance. Interestingly, we do not see this effect in the corresponding  $\Delta^{13}\text{C}$  values. The reduced stomatal conductance due to salinity stress seems to dominate the discrimination against  $^{13}\text{C}$ , masking the opposite effect of the DIC taken up by the plants.

Clearly, our plant growth experiment under two different spray water regimes (group 1 vs. group 2) seem to indicate two different reactions of the plant metabolism. Plants of group 1 treatments, sprayed with increasing amounts of mineral (including DIC), enriched non-salty tap water, indicate that plants react with increasing stomatal closure, limiting thereby access of atmospheric  $\text{CO}_2$ . As a result, discrimination against the heavier carbon isotopes decreases. At certain DIC concentrations and with additionally increasing salinity levels (group 2), stomatal closure must be so tight that the only remaining carbon source for plant tissue formation via photosynthesis could be the DIC originating from the irrigation water or the mixture of irrigation and spray water, as indicated by the apparent large proportion of carbon in plant tissues of group 2 treatments G-5 and G-6 originating from DIC (Figure S4, Table 2). This is also reflected by the large discrimination of the plants of G-5 and G-6 against atmospheric  $^{14}\text{C}$ , but comparably low discrimination against water  $\text{DI}^{14}\text{C}$  (Figure 4, Table 3). To some extent, treatment G-2, sprayed with (non-salty) water containing very high mineral salt concentration (including DIC) seem to indicate a similar process as seen in salt-water sprayed treatments (G-5 and G-6).

G-2 plants (“>marine”) exhibit a  $^{14}\text{C}$  concentration which is distinctly too depleted, namely  $0.9736 \pm 0.0027$  (Table 2). As the corresponding spray water contained only traces of  $\text{NaCl}$  (see Table 1), this shift cannot be explained by salinity stress. The plants of G-2 faced several types of stress, including  $\text{HCO}_3^-$  stress, relevant for the present study:

Stomatal closure is not only caused by salinity but also by high  $\text{CO}_2$  or  $\text{HCO}_3^-$  concentrations. The critical concentration level is probably species-specific (see, e.g., Engineer et al. 2016; Kolla et al. 2007; Misra et al. 2015; Mrinalini et al. 1982; Tian et al. 2015). Under high  $\text{HCO}_3^-$  concentration, the excess  $\text{HCO}_3^-$  can also be excreted via the roots (Poschenrieder et al. 2018).

G-2 plants discriminate about twice as much against atmospheric  $^{14}\text{C}$  (ca. 32‰) than against atmospheric  $^{13}\text{C}$  (ca. 18.05‰), as would be expected for, e.g., chemical processes (O’Leary 1981; Stern and Vogel 1971). Although the  $\text{Na}^+$  and, in particular,  $\text{Cl}^-$  concentration of the spray water of G-2 plants was higher than that of the G-1 plants, there is no further decrease in discrimination compared to G-1

plants (see Table 2). Instead, high  $\text{HCO}_3^-$  concentration in the spray water results in increased intercellular partial pressure of  $\text{CO}_2$ , due to the conversion of  $\text{HCO}_3^-$  to intercellular  $\text{CO}_2$  by carbonic anhydrases, and, thus, an increased  $p_i/p_a$  ratio. The resulting high  $p_i$  is reflected by an increased discrimination against both  $^{13}\text{C}$  and  $^{14}\text{C}$  (see Figure 6).

The proportion of  $^{14}\text{C}$  in plants originating from DIC is remarkably high (see Table 2), especially for the plants of the treatment groups G-5 (Schlei water; ca. 53%) and G-6 (Baltic Sea water; ca. 67%). The observed DIC effect and the underlying mechanisms seem to be similar to the freshwater reservoir effect observable in, e.g., aquatic plants (e.g., Ascough et al. 2007; Geyh et al. 1998; Philippsen 2013). Freshwater bodies can show a (variable) depletion in  $^{14}\text{C}$ , resulting from the input of groundwater containing DIC originating from the dissolution of calcareous bedrock, old soil carbonates, and geothermal processes (e.g., Ascough et al. 2007; Geyh et al. 1998; Philippsen 2013). The  $^{14}\text{C}$ -depleted DIC, incorporated by the plants, has a distinct impact on the radiocarbon concentration of the plants and also enters the food chain, thus affecting the radiocarbon concentration of consumers of freshwater food. However,  $\text{DI}^{14}\text{C}$  can also affect the radiocarbon concentration of terrestrial plants.

As demonstrated by  $^{14}\text{C}$  tracer studies, the uptake of  $\text{H}^{14}\text{CO}_3^-$  into plant tissues depends on various factors, including its concentration (e.g., Pelkonen et al. 1985; Vapaavuori and Pelkonen 1985; Viktor and Cramer 2005), the overall nutrient supply (e.g., Werth and Kuzuyakov 2005), and physiological factors such as water stress (e.g., Bota et al. 2004). Distinct species-differences (e.g., Pelkonen et al. 1985) as well as differences between bicarbonate uptake in different plant organs or compounds are observable (e.g., Bialczyk and Lechowski 1992; Domanski et al. 2001; Pelkonen et al. 1985; Vapaavuori and Pelkonen 1985; Werth and Kuzuyakov 2005; Zamanian et al. 2017). Accordingly, the published proportion of  $^{14}\text{C}$  derived from carbonates and incorporated in plant tissues varies.

Schäfer (1988) observed that after root labeling with  $\text{NaH}^{14}\text{CO}_3$  almost 50% of the  $^{14}\text{C}$  was incorporated into the sugar and starch fraction of spring wheat (*Ador* sp.). Acid-stable plant products (= excluding inorganic carbon) contained up to 79% of  $^{14}\text{C}$  taken up from the medium labeled with  $\text{NaH}^{14}\text{CO}_3$  in willow (*Salix aquatic gigantean*) and up to 63% in sunflower (*Helianthus annuus*) plants (Pelkonen et al. 1985; Vapaavuori and Pelkonen 1985). The proportional contribution of root-derived  $^{14}\text{C}$  to leaf total photosynthesis in paper mulberry (*Broussonetia papyrifera*) was about 28%, measured 10 and 20 days after treatment. In contrast, for white mulberry (*Morus alba*) after 10 days about 8% DIC input was measured, while it was 0% after 20 days due to low root-zone bicarbonate concentration (Wu and Rao 2023; Wu and Xing 2012).

Zamanian et al. (2017) investigated root- and shoot-labeled field gromwell (*Buglossoides arvensis*), growing on sand and loess soil, respectively. Fruits of plants growing on calcareous soil exhibit apparent  $^{14}\text{C}$  ages which are overestimated by several hundred years. The proportion of  $^{14}\text{C}$  taken up from soil pore water containing dissolved carbonates and stored in fruit carbonates was estimated to about 6% (Zamanian et al. 2017), thus, much lower than for our plants growing under salinity stress (ca. 53% (G-5) and 67% (G-6); Table 2). The physiological stress conditions of the G-5 and G-6 plants most likely enhanced the uptake of DIC (see above), thus resulting in the observed high  $\text{DI}^{14}\text{C}$  proportions. This example actually demonstrates the large effect of the uptake of even a small proportion of  $\text{H}^{14}\text{CO}_3^-$  on the  $^{14}\text{C}$  concentration in plants (Zamanian et al. 2017). The available proportion of  $\text{DI}^{14}\text{C}$  in the spray water of both G-5 (Schlei water; 125.6 mg/L) and G-6 (Baltic Sea water; 79.6 mg/L; see Table 1) was higher than that in the calcareous soil in the study by Zamanian et al. (2017;  $\leq 13$  mg/L). Seawater usually contains  $\text{HCO}_3^-$  levels of about 140 mg/L (Wright and Colling 1995b). The  $\text{HCO}_3^-$  concentration in the spray water of G-2 was even higher (ca. 191 mg/L  $\text{HCO}_3^-$  in mineral salt (Göhring et al. 2023a), equivalent to about 436 mg/L  $\text{CO}_2$  after dissolving the mineral salt in tap water G-0).

The resulting shift in the  $^{14}\text{C}$  concentration due to the admixture of assumed  $^{14}\text{C}$  free fossil carbon in G-6 (measured  $\text{F}^{14}\text{C}$  0.9581) vs. the contemporary atmospheric carbon concentration ( $\text{F}^{14}\text{C}$ : 1.0044) with a calculated fossil carbon contribution of about 4.6% (see Figure 5 and Table 2) due to salinity or  $\text{HCO}_3^-$  stress is similar to the shift observed by Zamanian et al. (2017) (ca. 500  $^{14}\text{C}$  years, equivalent to about 6% in  $\text{F}^{14}\text{C}$ ), resulting from the uptake of soil carbonate derivatives. It is conceivable that the actual shift, caused by either a direct or an indirect sea spray effect, could be even higher than observed

in this pilot study. However, both the observed results and the potential variation in the  $\text{DI}^{14}\text{C}$  contribution of coastal plants needs to be further verified in the future. Besides the sea spray effect, our findings also suggest that changes in the isotopic composition or ion concentration of groundwater, respectively pore water can affect the radiocarbon data of the investigated plants. A changed proportion of  $^{14}\text{C}$  from DIC taken up by the plants causes shifts in the radiocarbon dating. This can, e.g., also be of interest for regions which are (regularly) flooded, not only by seawater but also by terrestrial aquatic sources with a depleted  $^{14}\text{C}$  signature. In addition, physiological reactions in plants, besides salinity and  $\text{HCO}_3^-$  stress, as a result from environmental conditions (e.g., temperature, solar radiation, precipitation, aridity/humidity, drought stress) may affect radiocarbon dating as well. This is especially true for those environmental factors influencing the stomatal conductance as well as the photosynthesis rate, also affecting the  $\delta^{13}\text{C}$  signature of plants (see section 1).

It is important to differentiate between an “indirect” sea spray effect which is caused by associated physiological reactions in the plants as a result from, e.g., salinity stress and a “direct” sea spray effect, caused by the uptake of ions of marine origin (aerosols). The indirect and direct sea spray effect can be distinguished with respect to the stable isotope fingerprints of the treated plants of group 1 and 2. A direct sea spray impact on the radiocarbon signature is visible by shifted radiocarbon concentrations towards values expected for seawater or similar to the marine spray water (see G-5 and G-6). Apparently, the plants of G-5 and G-6 take up a calculated proportion of (old) fossil  $^{14}\text{C}$  of about 3.7% and 4.6%, respectively, incorporated in the plants (Figure 5, Table 2). Comparison of the fossil  $^{14}\text{C}$  contribution in control plants G-4 (0.2%) with that in G-5 and G-6 plants suggests that the fossil  $^{14}\text{C}$  signal detected in the plant tissue of G-5 and G-6 originates from the spray water, whereas the signal in the corresponding control groups can be understood as atmospheric (or irrigation water) background noise with only low anthropogenic impact, relative to the HPB atmospheric data. Our values are distinctly lower than those observed for industrial (urban) regions with values of even 10% (e.g., Varga et al. 2019). The fossil  $^{14}\text{C}$  signal in seawater, resulting in the marine reservoir effect (see section 1), also slightly affects the plants of treatment group 2, which were sprayed with brackish water from the Baltic Sea and the Schlei inlet, which is fed by Baltic Sea water, thus contributing to the overall fossil  $^{14}\text{C}$  contribution in the plants. We can see smaller such values for plants of treatment group 1, nevertheless, a distinct uptake of fossil  $^{14}\text{C}$  cannot be demonstrated with the current experimental settings (see Figure 4, Table 3). Using (much) older tap water for both irrigation and spraying (mineral salt solutions) than the used Munich tap water could result in clearer results with respect to fossil  $^{14}\text{C}$ , thus, for differentiating between the indirect and direct sea spray effect on radiocarbon analyses. As outlined above, the  $\Delta^{14}\text{C}$  values of the plants of the treatment groups G-5 and G-6 are mainly affected by the uptake of  $^{14}\text{C}$  from DIC (and respective  $\text{DIC}/\text{HCO}_3^-$  concentration levels; see also Figures S2B and S4). The applied spray water results in reduced stomatal conductance, which in turn causes a decrease in carbon isotopic discrimination against both  $^{13}\text{C}$  and  $^{14}\text{C}$ , also documented by decreased  $\Delta\Delta^{14}\text{C}/\Delta^{13}\text{C}$  ratios (Table 3). At the present stage of research, it is not possible to clearly distinguish between the influence of DIC in irrigation water and in spray water (Schlei water, Baltic Sea water). However, it seems likely that the higher  $\text{HCO}_3^-$  levels as well as the lower  $^{14}\text{C}$  concentrations in the spray water have a higher impact than tap water used for irrigating the plants. Nevertheless, further experiments are required to verify the impact of both spray and irrigation water.

It became apparent that the tap water used for spraying the control groups (G-0/G-4) or used for the preparation of the mineral salt solution for group 1 treatment, taken in the laboratory, was different from tap water used for irrigating all plants (G-GW), taken in the climate chamber of the greenhouse. This is not only the case with respect to the stable isotope data ( $\delta^{13}\text{C}_{\text{DIC}}$ : G-0/G-4:  $-4.6\text{‰}$ , G-GW:  $-3.6\text{‰}$ ;  $^{87}\text{Sr}/^{86}\text{Sr}$ : G-0/G-4: 0.708335, G-GW: 0.708280; Table S1) and the (trace) elemental composition (e.g., [Ca]: G-0/G-4: 99.51 mg/L, G-GW: 50.49 mg/L; [Sr]: G-0/G-4: 181.82  $\mu\text{g/L}$ , G-GW: 157.78  $\mu\text{g/L}$ ; see also Göhring et al. 2023a), but also with respect to radiocarbon dating (G-0/G-4:  $678 \pm 26$  BP, G-GW:  $551 \pm 27$  BP) or  $\text{F}^{14}\text{C}$  (G-0/G-4:  $0.9191 \pm 0.0029$ , G-GW:  $0.9337 \pm 0.0031$ ). Laboratory and greenhouse were located in two adjacent buildings of the LMU Biocenter, obviously

using different water pipes, i.e., galvanized pipes in the laboratory building (containing traces of Zn and Pb). The measured calcium as well as DIC concentration for G-0/G-4 ([Ca]: 99.51 mg/L, [DIC]: 298.4 mg/L) and G-GW water ([Ca]: 50.49 mg/L, [DIC]: 162.5 mg/L; see Table 1 and Göhring et al. 2023a) also points to differences in the overall calcium carbonate concentration in the two tap water sources. Furthermore, the residence time of the water in the pipe of the greenhouse chamber was most likely different from that in the pipe of the laboratory, located in different buildings and at different floors. It also has to be emphasized that the presented isotopic composition of the irrigation water samples and the tap water used to prepare the mineral solutions of group 1 and for spraying the control groups could have (slightly) varied over the growth experiment. However, all variations would have equally influenced all plants, including the control groups.

#### 4.2 Dealing with the marine reservoir effect and the sea spray effect in $^{14}\text{C}$ data

The magnitude of the salinity-induced (indirect) sea spray effect, visible in plants grown under salinity stress (G-5 (“Schlei”):  $269 \pm 22$  BP; G-6 (“Baltic”):  $344 \pm 23$  BP; see section 4.1), is comparable to the (modern) marine reservoir age of the Baltic Sea ( $273 \pm 18$   $^{14}\text{C}$  years) as determined by Fischer and Olsen (2021) or the (pre-bomb) seawater reservoir age in the Western Baltic Sea of about 445  $^{14}\text{C}$  years (Stuiver and Reimer 1993; Heaton et al. 2023; 2020). Since our analyses are based on a very small dataset, these findings are not yet valid. Nevertheless, our data imply that the sea spray effect on  $^{14}\text{C}$  might behave in a similar way as a reservoir effect, with certain dependence on physiological reactions in the plants (see section 4.1).

Consumption of marine food sources by humans is known to affect the radiocarbon dating of these humans (marine reservoir effect; see section 1). Humans - or omnivores in general - living in coastal regions or obtaining their food from such regions can show a  $^{14}\text{C}$  age intermediate between that of marine mammals (e.g., seal) and terrestrial herbivorous mammals (e.g., deer), depending on their dietary composition (see, e.g., Yoneda et al. 2002).

A marine impact on  $^{14}\text{C}$  is commonly controlled by investigating the  $\delta^{13}\text{C}_{\text{collagen}}$  and  $\delta^{15}\text{N}_{\text{collagen}}$  values which, beyond others, can give information on the consumption of marine protein sources (see section 1). Based on the isotopic signature of these two isotopic systems, terrestrial herbivores are supposed to be unaffected by the marine reservoir effect and radiocarbon data are corrected against the calculated marine reservoir age based on a marine and terrestrial end member (see, e.g., Ascough et al. 2005; Cook et al. 2015; Dury et al. 2018; Sayle et al. 2014). However, even if herbivorous mammals have not consumed any marine food, there can be a marine bias due to the consumption of plants influenced by the sea spray effect. So far, the marine impact on terrestrial samples caused by sea spray aerosols has not been addressed.

The sea spray signal enters the isotopic fingerprint along the terrestrial food chain. Accordingly, this impact must not be ignored in both stable isotope as well as radiocarbon analyses. Neither  $\delta^{13}\text{C}_{\text{collagen}}$  nor  $\delta^{15}\text{N}_{\text{collagen}}$  are capable of giving hints on a potential sea spray impact as no marine but terrestrial protein (e.g., terrestrial plants) is consumed in such a case (Göhring et al. 2018; Göhring et al. 2020). Accordingly, investigating only these two isotopic systems would be insufficient at coastal sites. For identifying a sea spray effect in archaeological skeletal remains, the investigation of additional isotopic systems is, thus, required. The sea spray signal in, e.g.,  $\alpha$ -cellulose carbon ( $\delta^{13}\text{C}_{\text{cellulose}}$ ) is, moreover, also transferred to the terrestrial consumer via the diet, resulting in a seemingly marine isotope signal in the  $\delta^{13}\text{C}_{\text{carbonate}}$  values of terrestrial animals as well as humans (Göhring et al. 2018, 2020). This was further evidenced in recent studies (Göhring et al. 2023a, 2023b). Accordingly, it is mandatory to control for the sea spray by measuring (several) other isotopic systems potentially affected by sea spray. By investigating both terrestrial herbivores and marine piscivorous mammals it is possible to identify a potential sea spray impact and correct for the sea spray also in human consumers (Göhring et al. 2018, 2020).

### 4.3 Potential implications for bioarchaeological studies

While our results have to be understood as preliminary data and require additional detailed investigations based on a larger dataset, the observed indirect sea spray effect on radiocarbon data of (modern) terrestrial plants, visible in  $F^{14}\text{C}$  as well as in the apparent  $^{14}\text{C}$  age, is of interest for archaeological studies in coastal regions. With respect to stable isotopes, the sea spray effect identified in the greenhouse experiments was also validated in environmental samples collected next to the Baltic coast (Göhring et al. 2023b). Thus, the greenhouse  $^{14}\text{C}$  data might be an indicator for the sea spray impact at coastal sites, as well.

Based on our preliminary results, we expect a reservoir age of about 250–290 years (see G-5, “Schlei”) for radiocarbon dating of plant samples from (or nearby) the archaeological site of Haithabu. In the case of archaeological material found in Haithabu (cal AD 804–1066) and its successor town Schleswig (Rathausmarkt site cal AD 1070–1210, St. Clements graveyard cal AD 1250–1350), located at opposing sides of the Schlei inlet close to the Baltic Sea (see, e.g., Grupe et al. 2013; Hilberg 2008; Jahnke 2006; Jankuhn 1986; Müller 2016; Schlesinger 1972), a sea spray-induced shift by about 200 or 300 years can actually be problematic.

For illustration, let us have a look at the shipwreck “Wrack 4” found in the harbor of Haithabu. The wood was  $^{14}\text{C}$ -dated to  $1024 \pm 25$  BP, calibrated to 987–1017 AD. Accordingly, this ship would be allocated to the Viking Age period. In contrast, dendrochronology determined that the investigated tree was logged around or after 1184 and, thus, during medieval times (Kalmring 2010; Nakoinz 2005; von Carnap-Bornheim et al. 2002; von Carnap-Bornheim et al. 2003). “Wrack 4” would be associated to Schleswig based on dendrochronology, while radiocarbon analysis points to an association with Haithabu. The difference between calibrated  $^{14}\text{C}$  dating and dendrochronology is 167 to 197 years. The  $^{14}\text{C}$ -dated ship planks (Nakoinz 2005) were made of oak wood (Crumlin-Pedersen 1969). Oaks grew locally in the region (see Behre 1983). Thus, the oakwood likely originated from the close vicinity of Haithabu/Schleswig. Accordingly, we suppose that the difference between radiocarbon and dendrochronological age could have been caused by the sea spray effect. For comparison, the artificial sea spray with Schlei water (G-5, expected Haithabu signal) resulted in a divergence of  $269 \pm 22$  years (247–291 years). This shift, based on greenhouse data, however, clearly has to be evaluated based on modern local samples.

## 5. Conclusion

European beach grass (*Ammophila arenaria*, L.), grown in planters in a greenhouse between June and December 2020, have been irrigated with tap water and sprayed with mineral salt solution, with low NaCl concentration but partly high concentration in, e.g.,  $\text{HCO}_3^-$ , as well as natural salty, i.e. NaCl enriched, water. By analyzing the carbon isotope inventory of irrigation and spray water as well as treated plants this study aimed to investigate possible reservoir age effects in grown plant tissues since all waters used were depleted in radiocarbon concentration in comparison to contemporary atmospheric  $\text{CO}_2$ .

Based on the presented preliminary results we observed a potential sea spray impact on the radiocarbon composition of terrestrial plants treated with an artificial sea spray, which is resulting from the uptake of  $^{14}\text{C}$ -depleted DIC as well as from physiological reactions in the plants and accompanied discrimination effects. We emphasize, however, that further analyses are required in order to verify a potential sea spray-induced reservoir effect as indicated by our study.

Measured carbon isotope composition in the plant tissue indicates two distinctively different effects. Group 1 plants grown under the influence of spray water enriched in minerals, including DIC, are depleted in  $^{14}\text{C}$ . Overall, the discrimination against atmospheric  $^{14}\text{C}$  relative to the discrimination against atmospheric  $^{13}\text{C}$  indicates a reduction in the stomatal conductance, probably caused by increasing DIC as well as  $\text{Na}^+/\text{Cl}^-$  contents in the spray water. In difference from the group 1 experiments, group 2 plants were sprayed with naturally salty (NaCl) water with lower DIC content

compared to the group 1 experiment. While discrimination against  $^{13}\text{C}$  was of comparable magnitude as seen for G-1 (“marine-like”), the discrimination against  $^{14}\text{C}$  increased markedly. Salinity stress also induces a reduced stomatal conductance, similar to the effect seen in group 1, but so intense that apparently DIC in the irrigation water as well as admixed spray water delivered the necessary carbon for plant growth, causing an apparent aging in plant tissue.

As a consequence, we want to emphasize that plants or terrestrial herbivores from coastal sites should not be used as a control for a 100% terrestrial  $^{14}\text{C}$  signal without checking stable or radiogenic isotopic systems besides  $\delta^{13}\text{C}_{\text{collagen}}$  and  $\delta^{15}\text{N}_{\text{collagen}}$  (e.g.,  $\delta^{13}\text{C}_{\text{carbonate}}$ ,  $\delta^{18}\text{O}_{\text{carbonate}}$ ,  $\delta^{18}\text{O}_{\text{phosphate}}$ ,  $\delta^{34}\text{S}_{\text{collagen}}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ). In addition, we want to point out that the sea spray signal in stable isotopic systems can be detected in samples located several kilometers, potentially even about several hundred kilometers distant from the shoreline (e.g., Alonzi et al. 2020; Göhring et al. 2023b; Kochergina et al. 2021; Nehlich 2015; Snoeck et al. 2020). Regional and seasonal differences could also have a distinct effect on the local sea spray signal (Göhring et al. 2023b).

Based on our presented preliminary results it is important to consider the sea spray effect when performing radiocarbon analyses on terrestrial individuals (plants, animals, humans) from coastal sites. They might be prone to a sea spray reservoir effect. Further (greenhouse) experiments for the quantification of the indirect as well as the direct sea spray effect in plants and animals are required in order to further reveal the reservoir effect on terrestrial individuals, including humans, caused by sea spray and associated physiological or metabolic reactions as well as to correct for the sea spray impact on radiocarbon analyses.

**Supplementary material.** To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2025.1>

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