INFLUENCE OF SALT MARSH ECOSYSTEM ON THE CONCENTRATION AND EMISSION OF CO_2 FROM THE WADDEN SEA COAST SOIL OF NORTHERN GERMANY

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Abstract

A field study was conducted to evaluate the possible factors controlling the fluxes of carbon dioxide along a toposequence of daily to seasonally flooded coastal salt marsh soils. The soil at the top end of the salt marsh (with a height of 1.8 m above sea level (a.s.l.) and a dense vegetation cover) was salic silty to clayic (Typic Sulfaquent), while the soil at the bottom end (with some salt bushes and a 1.4 m a.s.l.) was sandy to silty (Haplic Sulfaquent). The mean (depth: 0 - 100 cm) values of pH were around 7, and of redox potentials (Eh) in the Typic Sulfaquent ranged from -162 to + 104 mV during all the seasons. The average net-emission of CO_2 (-14.0 g m^{-2} a^{-1}) above the vegetation cover was negative for the Haplic Sulfaquent but highly positive for Typic Sulfaquent round the year (857 g m^{-2} a^{-1}). The average maximum concentrations of CO_2 were detected within the surface soils 20 to 40 cm in both the profiles. In the surface soils of 0 to 20 cm the concentrations of CO_2 measured were relatively low though the values were about 5 to 20 times higher than that of the atmospheric (0.35 g/v) concentration. For the average of two Haplic Sulfaquents, the soil temperatures were almost 2°C higher than that of the Typic Sulfaquent and it was also 2.5°C higher than the mean annual temperature (9.5°C) of the soils. The current results show that the CO_2 fluxes seasonally varied significantly and for certain periods of the year the coastal salt marsh soils can act either as a sink or source for atmospheric CO_2 depending on the physical and chemical properties of the soils.

Key words: Coastal salt marsh soils, concentrations and emissions of CO_2, factors controlling fluxes of CO_2, redox potentials

Introduction

Scientists have observed that carbon dioxide concentrations in the atmosphere have been increasing significantly over the past century, compared to the pre-industrial era (about 280 ppm: IEA 2015). The IEA also reported that in 2014, the concentration of CO_2 (397 ppm) was about 40% higher than in the mid-1800s, with an average growth of 2 ppm/year in the last ten years. In 2013, global CO_2 emissions reached 32.2 Gt CO_2, an increase of 2.2% over 2012 levels. This was higher growth than in 2012 (0.6%), but lower than the average annual growth rate since 2000 (2.5%).

Consistent with the intergovernmental panel on climate change (IPCC) guidelines for national green house gas (GHG) inventories and the annual GHG inventories submitted by the U.S. and other nations to the United Nations Framework Convention on Climate Change (UNFCCC), the

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biofuel components of fuel combustion CO_2 emissions are classified as 'biogenic CO_2' and are tracked separately as informational items. This change in classification allows for a more accurate comparison of GHG inventory with other subnational and national GHG inventories, which follow the same IPCC guidelines (CEPA 2016).

Trace gases are becoming more and more interesting due to their possible contribution to an enhance greenhouse effects. The fluxes of carbon dioxide from soil are an important part of the terrestrial carbon budget and the global carbon cycle (Batracharya *et al*. 2000). As soils of coastal areas are emittants of CO_2 due to their high content of organic matter. It is not yet clear that at what extent of CO_2 is adding from these soils to the CO_2 content of the atmosphere. Coastal salt marsh soils may be a potential source or sink of CO_2 due to having the oxidation-reduction processes as a result of frequent tidal influences. As soils differ in their characteristics, it is expected that CO_2 emissions from soils also differ according to particular properties of the soils. Carbon dioxide develops under oxic as well as under anoxic soil conditions and also faces CO_2 reduction (Hou *et al*. 2000). It is obvious that the factors affecting CO_2 emissions are complicated and interrelated.

Coastal salt marsh soils play an important role in sequestration of atmospheric carbon, as well as in the emission of radioactively active trace gases. Agricultural practices contribute an estimated 25% of total anthropogenic emission of CO_2 and could contribute between 28 and 33% of the radioactive forcing in this century if emission of this gas is doubled (Duxbury 1995). Under the Kyoto Protocol, the European Union is committed to an 8% reduction in CO_2 emissions, compared to baseline (1990) levels, during the first commitment period of 2008 - 2012 (Smith *et al*. 2000). Therefore, it is very essential to know the potential sources and sinks of the CO_2 in order to take authentic mitigation programmes. Investigations on the sources, sinks and factors regarding the emission of CO_2 and its concentration throughout the soil profiles especially in coastal or young marine soils are still insufficient. Accordingly, the present research was mainly focused on the emission and concentration of CO_2 and relevant parameters like redox potential throughout the profiles of salt marsh soils, which developed from the marine sediments as influenced by tides of the North German Wadden Sea.

Materials and Methods

Study site: Field study was conducted near Soenke-Nissen-Koog in Schleswig-Holstein (Germany) during 2000-2001. The possible factors (Table 1) controlling the parameters regarding CO_2-dynamics along a toposequence of daily flooded to seasonally flooded coastal salt marsh soils were studied. The toposequence of the site is divided into three sectors (Table 1). The soil at the top end of the salt marsh was classified as salic silty to clayic Typic Sulfaquent (Salzrohmarsh), which is flooded (1.8 m a.s.l. or 0.15 m above mean high tide) for about 180 times in a year. This sector is covered with small (3 - 20 cm) vegetation (*Puccinellia maritima* along with some halophytes), which is extensively grazed by sheep during summer. While the bottom end of the site is flooded (1.4 m a.s.l. or 0.25 m below mean high tide) for about 700 times throughout the year. The soil

nearly middle of the toposequence was flooded for about 600 times, vegetation were mainly *Spartina anglica* and *Salicornia europea*, and was classified as sandy to silty Haplic Sulfaquent (Übergangsmischwatt: for this study, Haplic Sulfaquent) and the soil at the bottom end is designated as Haplic Sulfaquent-1.

Investigation and analysis: During gas measurements, the Haplic Sulfaquents were water saturated round the year, except for the first few cm which were unsaturated for about 1 to 2 hours during low tides. The top soil of Typic Sulfaquent was unsaturated especially during the vegetation period. This means that only coarse pores were free of water and the interior of the aggregates might have reduced conditions throughout the year.

Emissions of CO_2 at the soil surfaces of the Typic Sulfaquent and the Haplic Sulfaquents were measured following chamber method (chamber was made by acrylic glass with a base of 990 cm^2 and a volume of 27 L (Hutchinson and Mosier 1981). The chambers were cooled with water filled copper tubes, which were connected with a heat exchanger and their constructions allowed themselves to follow the variations in water tides. Three replications were considered in addition with a chamber, which was not connected with the soil and used as reference. The gas was collected for every 1 to 2 hours together with a lifting of the chambers depending on the temperatures for 24 to 48 hours at different seasons.

In order to measure the concentrations of CO_2 at the soils, one Typic Sulfaquent and two Haplic Sulfaquent soils from the above mentioned sites (Table 1) were collected and investigated under *in situ* conditions at different depths of the soil profiles by using aluminum-tube with a diameter of 10 cm. The tubes were installed by pressing (somewhere drilling) towards the depths of about 30 to 100 cm as required leaving no space inside the tube. The soil monolith inside the Al-tube was sectioned at every 10 cm by using tube cutter and both ends of the tube were closed and sealed immediately by Polyethylene (PE) lid, which were mounted by Para film. The lid on the head-end of each section of the tube was provided with an opening where a three-way valve was connected for gas collection. The gas was then collected by the process of evacuation through a 100 mL syringe, which was connected to each valve as mentioned above. The samples were then stored in cooling box and were analyzed within 48 hours. The gas samples were analyzed with a Shimadzu GC-14 with LC10 equipped with FID and ECD. Separation was done with a 3 m stainless steel column Porapack QS 80/100.

Water content of the initial soil sample was determined at each sampling time. The three replications for each site towards each depth had been considered for this study. Temperature sensors measured soil temperatures and redox potentials were determined with stationary platinum electrodes against Ag/AgCl-electrodes at different depths of the studied soils and the normal hydrogen electrode corrected the values.

Results and Discussion

Redox potential and soil temperature: The mean values of redox potentials (Eh) in the Typic Sulfaquent were ranged from –66 to +104 and were negative towards the deeper depth during all

the seasons except for the surface soils during summer, where the mean value was +104 mV (Table 2). The standard deviations (Sd) also varied widely and were more pronounced during summer followed by autumn. The Eh in the upper 3 cm of the surface soils of Haplic Sulfaquent varied mostly and the mean values ranged from 12 to 33 mV, except for the summer (–19 mV). Due to tidal influences and permanent water saturation beneath the thin layer of top soils in both the sites, the Eh values were obtained always negative and varied widely in most of the seasons. And the variations were more pronounced in the Haplic Sulfaquent round the year (Table 2). No continuous data were available for the Haplic Sulfaquent-1, and soil was strongly reduced below the upper from 0.5 to 1 cm similar (around –100 mV) to that of the Haplic Sulfaquent. The rH values (Table 1) in the epipedon of the Haplic and the Typic Sulfaquents ranged from 14.4 to 17.3 (corresponding with a grayish green to olive color of the soil matrix together with reddish brown holes), and in the sub-soils from 8.1 to 11.9 (corresponding with a black soil color due to sulfide). The rH values < 13 normally corresponds with a black color due to the formation of sulfide, and values < 10 make possible methane formation, whereas the values in between 13 and 20, Fe^{3+} can be reduced and Fe II/Fe III oxides led to the formation of so called blue green rust, together with reddish brown ferrihydrite along holes of soil animals and plant roots.

The Haplic Sulfaquent and Haplic Sulfaquent-1 soils were found to have almost similar chemical and physical conditions. Hence, the average values of their several parameters are presented as Haplic Sulfaquent in the Tables 1 and 2. The mean values of soil temperatures were in the range of 9.0 to 9.8°C for Typic Sulfaquent at depths of 0 to 100 cm and 10.1 to 12.0°C for Haplic Sulfaquent at depths of 0 to 50 cm round the year (Table 2). The higher temperatures at the later especially during summer seem to be influenced by daily flooding with relatively warmer sea water. Seasonal maximum mean soil temperatures were recorded during summer followed by autumn for Typic Sulfaquent and summer followed by spring for Haplic Sulfaquent. The average temperatures of the soils were found to have decreased towards the lower depths during spring and summer, and increased slightly during autumn and/or winter due to high heat capacity of the soils. And the trend was more pronounced with the Haplic Sulfaquents where the soil temperatures were almost 2°C higher than that of the Typic Sulfaquent (Table 2) and it was also 2.5°C higher than the mean annual temperature (9.5°C) of the soils. This increment of temperature might be due to higher absorption of solar radiation by the almost bare and more salt saturated surface of the Haplic Sulfaquent soil as well as influenced by the warmer surface sea water intrusions. Almost similar trend of increment of mean annual soil temperature was also observed for watten soils of the National park in Schleswig-Holstein (Becker 1998).

Emissions of CO_2: The average net emissions of CO_2 (–14.0 g m^{-2} a^{-1}) was obtained negative (Table 3) for Haplic Sulfaquent though the emissions of CO_2 was measured positive only during summer. The negative values of CO_2 emissions of the soils are the result of a high solubility of CO_2 in water together with a high translocation of emitted CO_2 by sea water. The negative values of CO_2 emissions also indicate that more CO_2 was fixed through photosynthesis than produced and emitted by plants catabolism and microbial activity. But in Typic Sulfaquent, the emissions of CO_2

Table 1. Some physico-chemical properties of salt marsh soils at the Wadden sea coast of Northern Germany.

Typic sulfaquent (Typishe salzrohmarsh): Vegetation - *Puccinellia maritima* along with some halophytes, about 180 flooding per year, strongly stratified.

Depth (cm)	Horizon (US Tax.)	rH# value	pH water (1 : 2.5)	*ECe (mS/cm)	Org.-C (g/kg)	Total-N (g/kg)	Bulk density (mg/m³)	Hydrolic con.(cm/d)	Munsell color
0 - 14	Azh	17.3 - 10.4	6.9	37.1	35	3.8	0.73	70.8	10YR 3/2
14 - 29	Czrg		6.9	36.9	27	2.8	0.81	47.2	10YR4/1+
29 - 45	Czgr		6.9	40.7	23	2.4	0.79	48.5	2.5YR4/6
45 - 70	Czr1	11.8 - 8.8	6.8	38.3	21	2.1	0.80	1.0	5gY4/1
70 - 120	Czr2	10.7 - 8.1	6.8	39.7	18	1.8	0.76	0.4	N1

Depth	Particle size (Int.) distribution (%)			CEC	Org.-C	Water content (%) at different pF values		
	Sand	Silt	Clay	c mol kg⁻¹	-∞	1.8	2.5	4.2
0 - 14	7.6	66.2	26.2	24.4	70.6	54.5	48.3	32.4
14 - 29	7.5	65.0	27.5	27.7	67.7	59.1	50.9	28.7
29 - 45	8.1	63.8	28.1	24.4	68.7	60.8	52.8	26.4
45 - 70	5.0	62.8	32.2	21.5	68.6	63.6	55.0	25.7
70 - 120	39.9	27.6	32.5	21.6	70.4	63.3	54.3	26.3

Haplic Sulfaquent (Marines Übergangsmischwatt): Vegetation - *Spartina anglica* and *Salicornia europea*, about 600 flooding per year, strongly stratified.

Depth (cm)	Horizon (US Tax.)	rH# value	pH water (1 : 2.5)	*ECe (mS/cm)	Org.-C (g/kg)	Total-N (g/kg)	Bulk density (mg/m³)	Hydrolic con.(cm/d)	Munsell color
0 - 3	Az(h)	15 - 13.6	7.0	41.6	12.0	1.2	1.16	67.6	5Y5/2 +
3 - 8	Czrg		7.0	39.8	6.0	0.7	1.16	67.6	5YR3/5
8 - 22	Czr1	11.9 - 8.8	6.9	39.1	5.8	0.6	1.22	77.2	N2 -
22 - 45	Czr2		7.0	42.4	5.9	0.6	1.17	95.7	5gY 4/1
45 - 85	Czr3	10.5-8.6	6.8	43.1	9.2	1.0	1.29	53.9	

Depth	Particle size (Int.) distribution (%)			CEC	Org.-C	Water content (%) at different pF values		
	Sand	Silt	Clay	c mol/kg	-∞	1.8	2.5	4.2
0 - 3	45.0	48.0	7.0	17.3	55.3	46.4	33.3	13.2
3 - 8	58.7	39.8	1.5	13.6	55.3	46.4	33.3	13.2
8 - 22	51.7	44.9	3.4	15.3	53.3	45.5	27.6	8.0
22 - 45	46.8	46.1	7.1	16.5	55.2	46.4	30.5	8.0
45 - 85	33.6	52.3	14.1	27.2	50.4	46.8	29.4	7.4

The rH value has been calculated from the formula of rH = (2 Eh/59) + 2 pH: Schlichting *et al.* 1995); values of mean quarternary redox potential of Table 2. *ECe = Electrical conductivity of saturation extracts.

Table 2. Mean seasonal (2000 - 2001) redox potentials and temperatures of salt marsh soils in the Wadden Sea coast of Northern Germany.

Depth (cm)	Redox potential (mV)								Temperature (°C)								Average Temp. (°C)
	Spring	Sd	Summer	Sd	Autumn	Sd	Winter	Sd	Spring	Sd	Summer	Sd	Autumn	Sd	Winter	Sd	
Typic Sulfaquent																	
10	−72	138	104	247	−66	185	−100	68	9.3	3.4	17.8	2.5	9.0	3.4	3.0	1.9	9.8
50	−97	47	−157	207	−128	54	−69	47	8.6	3.2	16.1	1.4	9.2	3.3	3.7	1.7	9.4
100	−113	43	−90	71	−138	61	−162	106	7.6	2.3	15.1	1.9	9.1	3.0	4.2	1.6	9.0
Haplic Sulfaquent																	
3	12	181	−19	129	33	199	26	138	12.1	5.5	23.4	4.0	8.2	4.4	4.1	2.0	12.0
25	−79	155	−147	34	−129	42	−65	74	9.1	5.0	20.4	3.9	7.4	3.0	3.5	1.6	10.1
50	−108	134	−91	135	−146	36	−92	59	8.5	5.1	19.1	3.0	8.7	3.9	4.0	1.5	10.1

Table 3. Mean seasonal (2000 - 2001) and calculated annual net emissions (mg m^{-2} h^{-1}) of CO$_2$ from salt marsh soils in the Wadden sea coast of Northern Germany.

Emissions of CO$_2$ (mg m^{-2}h^{-1})

Soil unit	Spring		Summer		Autumn		Winter		Emission rates	
	CO$_2$	Sd	CO$_2$	SD	CO$_2$	Sd	CO$_2$	Sd	mg m^{-2} d^{-1}	g m^{-2} a^{-1}
Haplic sulfaquent	−3.19	55	7.7	102	−2.0	56	−8.9	26	−38.4	−14.0
Typic sulfaquent	33.6	93	116	193	196	234	45.5	86	2350	857

Level of significance

U-test	Haplic sulfaquent				Typic sulfaquent		
	Spring	Summer	Autumn		Spring	Summer	Autumn
	CO$_2$	CO$_2$	CO$_2$		CO$_2$	CO$_2$	CO$_2$
Summer	0.190				1.650*		
Autumn	0.468	0.158			3.193***	1.507	
Winter	0.350	0.008	0.516		0.771	0.741	2.494**

Level of significance: * = 90 %, ** = 95 % and *** = 99 %.

were highly positive round the year (857 g m^{-2} a^{-1}) in comparison to the Haplic Sulfaquent (–14.0 g m^{-2} a^{-1}), which might be due to high temperature, less flooding and the extremely low vegetation cover of the first as well as the activities of both micro flora and fauna, soil physical parameters, etc. of the salt marsh soils. The present findings of CO_2 emissions can be compared with the results of Scala *et al.* (2000) who measured CO_2 emissions ranged from 137 to 3455 g m^{-2} a^{-1} during November, 1998. Howard and Howard (1993) also proved a strong dependence of soil CO_2 emissions on soil temperature and water content.

The cracks have facilitated a quick escape possibility of the gas. The seasonal fluctuations of the emissions of CO_2 were highly significant for the Typic Sulfaquent soil (Table 3). These suggest that the vegetation cover, activities of soil flora and fauna, soil temperature and organic matter status are the main controlling factors for these trace gases.

Concentrations of CO_2: The concentrations of CO_2 varied strikingly throughout the soil profiles as well as with the seasons of the year (Fig. 1). The maximum average concentrations of CO_2 were measured during June, 01 (16.09 g kg^{-1} soil v.) followed by May, 01 (7.44 g), September, 01 (4.49 g) and August, 01 (4.42 g kg^{-1} v.) in the Typic Sulfaquent Soil. But the sequences of concentrations of CO_2 were June'01 (4.75 g) > September, 01 (3.31 g) > May, 01 (2.10 g) > August, 01 (1.32 g kg^{-1} v.) for the Haplic Sulfaquent soil and May (2.15 g) > September, 01 (1.36 g kg^{-1} v.) for Haplic Sulfaquent-1 soil. However, the average maximum concentrations of CO_2 were detected within the surface soils of 20 to 40 cm in both the profiles regardless of the seasons, except for the August, 01 where the maximum concentration was measured at a depth of 50 to 60 cm of the profile of Typic sulfaquent soil. The surface soils of 0 to 20 cm, the intensively rooted zone where the concentrations of CO_2 were measured relatively low though the values were about 5 to 20 times higher than that of the atmospheric (0.35 g l^{-1} v.) concentration.

The high concentration of CO_2 in the Typic Sulfaquent soil might be the results of dissimilatory processes of the plants as well as the higher activities of soil organisms. On the other hand, the stronger tidal influences at the Haplic Sulfaquent soils lead to dissolution of produced CO_2 and thereby can be considered as a sink of CO_2. Partial water saturation of the soil leads to low air conductivity, which concentrated the gases in the soil air and soil solutions. The low CO_2 concentrations in the reduced subsoil of all the soil profiles reflect the low microbial activity. Moreover, the low concentrations in the lower depth of Typic Sulfaquent soil might also be resulted from intensive exchange towards upward air pores where the higher concentrations were measured. These interchanges were enhanced by the extreme dryness during August resulted soil cracking down to the depths of about 30 cm, which was the reason for high concentration of CO_2 at a depth of 50 to 60 cm.

High temporal and spatial variations in the CO_2 emissions led to question whether the emission pattern reflects the concentrations of this gas in the soil. The highest concentrations at each sampling times were measured in the Typic Sulfaquent soil and the lowest concentrations were in the Haplic Sulfaquent soils, which were almost in the range of atmospheric concentration. Stratification, aggregation and/or variable pore volume with different continuity may lead to an

inhomogeneous soil with the formation of traps where produced CH_4 is accumulated leading to discontinuous release by bubbling (Takai and Wada 1990). In the permanent saturated soils, tidal marine water mixes and dilutes the gas content in the soil solution twice a day. Therefore, the
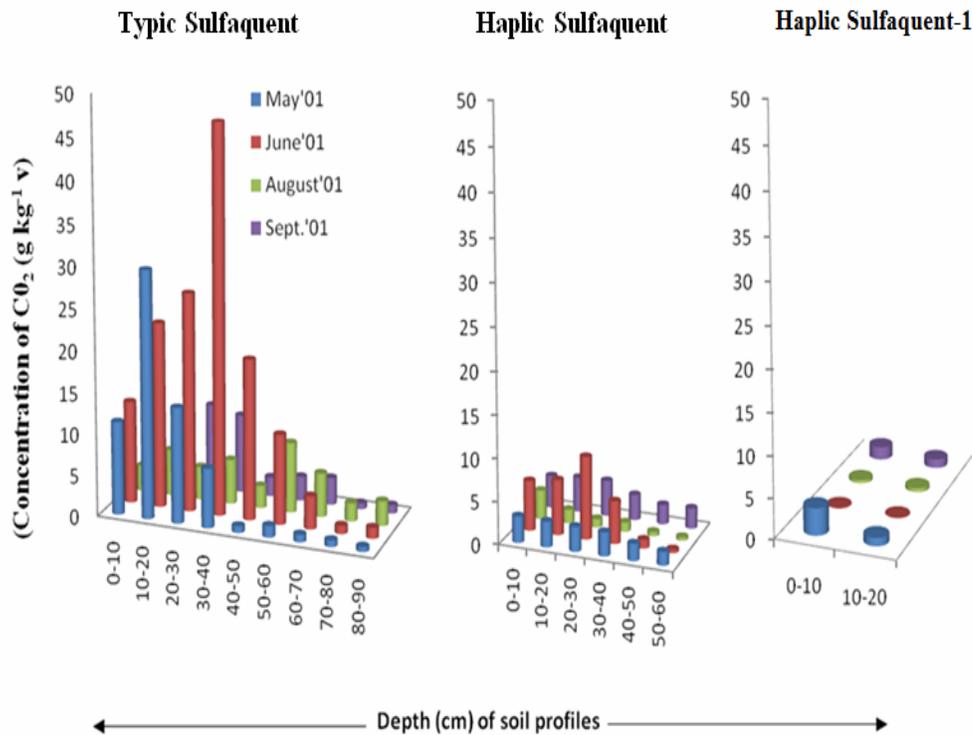
Fig. 1.   Concentration of CO_2 throughout the profiles of saltmarsh soils at different times as influenced by the ecosystems of Wadden sea coast of Northern Germany.

Haplic Sulfaquents have comparatively low gas concentrations to that of the Typic Sulfaquent, which mean not to build up. In the Haplic Sulfaquent soil, the shifting water table at rising tide may press the gas loaded water upward without exporting the soil solution from the system as the hydraulic conductivity of 68 to 96 cm/d in the upper soil which is much lower than the rising tide, leading to an enclosure of the entrapped soil solution.

Conclusion

The present study demonstrates that the CO_2 fluxes varied significantly among the seasons, which also shows that for certain periods of the year the coastal salt marsh soils can act either as a sink or source for atmospheric CO_2 depending on the nature of the soils. Relatively high net emission of CO_2 from the Typic Sulfaquent under salt meadow was due to high microbial activities as induced by easily decomposable organic matter of the sediments. This should be similar in the Haplic

Sulfaquent but a large amount of the CO_2 formed was dissolved into the sea water. Further research should be focused on more detailed look on the geophysical conditions of the soils regarding unpredictable concentrations and emissions of the CO_2 in different seasons.

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