



BCSIR

Available online at www.banglajol.info

Bangladesh J. Sci. Ind. Res. 52(3), 177-186, 2017

BANGLADESH JOURNAL
OF SCIENTIFIC AND
INDUSTRIAL RESEARCH

E-mail: bjisir07@gmail.com

Fluxes of methane and distribution of sulfate as influenced by coastal salt-marsh soil ecosystem of Northern Germany

H. R. Khan

Department of Soil, Water and Environment, University of Dhaka, Dhaka 1000

Abstract

The study was conducted in Schleswig-Holstein at the Wadden sea coast of Northern Germany to evaluate the possible factors controlling methane (CH_4) and sulfate (SO_4) dynamics 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 in the Typic Sulfaquent were ranged from -162 to +104 mV during all the seasons. The annual average emissions of CH_4 were almost 10 fold higher ($0.3 \text{ g m}^{-2} \text{ a}^{-1}$) in Haplic Sulfaquent than that ($0.03 \text{ g m}^{-2} \text{ a}^{-1}$) of the Typic Sulfaquent. In all the profiles, the concentrations of CH_4 were very low and varied significantly ($p \geq 0.05$) with the seasons and soil depths. The concentrations of CH_4 showed no dependence to temperature. The SO_4 contents were observed maximum in the Typic Sulfaquent followed by Haplic Sulfaquent during all the seasons. There is no noticeable correlation was obtained between the SO_4 and CH_4 concentrations. Moreover, even CH_4 was determined at depths where the SO_4 concentration in the soil solution was around $1200 \text{ mg SO}_4 \text{ L}^{-1}$.

Keywords : Coastal salt marsh soils; Concentrations and emissions of CH_4 ; Factors controlling CH_4 and SO_4 dynamics, Redox potentials

Introduction

Methane is a greenhouse gas, which's a 100-year time horizon Global Warming Potential (GWP) is 28 times that of carbon dioxide (IPCC, 2013). Methane is emitted by both anthropogenic activities and natural biogenic processes. The main anthropogenic emission sources are fugitive emission from solid fuel, leaks from gas extraction and distribution, agriculture, and waste management. Anthropogenic CH_4 emissions are assumed to account for more than half of the total CH_4 emissions from land and ocean (Voulgarakis *et al.*, 2013). Anthropogenic CH_4 emissions have increased significantly since pre-industrial times and rice fields corresponding to the increase in human population (Ghosh *et al.*, 2015), which resulted in a steep increase in atmospheric CH_4 concentration.

Soils of coastal areas are emittants of CH_4 due to their high content of organic matter and reduced conditions; it is not yet clear that at what extent of this gas is adding from these soils to the CH_4 gas content in the atmosphere. Coastal salt marsh soils may be a potential source or sink of CH_4 due to having the oxidation-reduction processes as a result of frequent tidal influences. There were large CH_4 concentrations in salting and in sulfate enriched hyper saline environments (Giani *et al.*, 1996). Moreover, as soils differ in their characteristics, it is expected that the emission of CH_4 from soil is also differ according to particular properties of the soils. Methane is

produced in anaerobic environments through either CO_2 reduction or transmethylation processes (Hou *et al.*, 2000). It is obvious that the factors affecting CH_4 emission are complex and interconnected. The redox potentials of less than -200 mV are the favorable condition for CH_4 formation (Conrad, 1989). On the other hand, Holmer and Kristensen (1994) suggested that there is a coexistence of sulfate reducing and CH_4 producing bacteria. Schipper and Reddy (1994) found high CH_4 concentration despite the higher SO_4 concentrations in the soil solution. King and Wiebe (1978) measured variations of CH_4 emissions in the range of 2 exponential powers in coastal salt marshes and these soils play an important role in sequestration of atmospheric carbon, as well as in the emission of radioactively active trace gases.

Methane emissions from natural wetlands account for around 30% of total CH_4 emissions (Voulgarakis *et al.*, 2013), which is one of the major source of natural biosphere CH_4 emissions. Emissions from natural biosphere sources have strong seasonal and interannual variability (Spahni *et al.*, 2011), contributing substantially to seasonal and interannual variability in atmospheric methane burden (Meng *et al.*, 2015). Agricultural practices contribute an estimated 65% of total anthropogenic emission of CH_4 and could contribute between 28 and 33% of the radioactive forcing in this century if emission of this gas is doubled (Duxbury, 1995). Therefore, it is very essential to

*Corresponding author e-mail: duharun@yahoo.com

know the potential sources and sinks of the CH₄ gas in order to take authentic mitigation programmes for this gas. Investigations on the sources, sinks and factors regarding CH₄ gas emission 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, concentration of CH₄ gas, distribution of SO₄ 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 Wadden Sea of Northern Germany.

Materials and methods

Study site

The study was conducted near Soenke-Nissen-Koog in Schleswig-Holstein at the Wadden sea coast of Northern Germany during 2000-2001. The possible factors (Table I) controlling the parameters regarding methane 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 around 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 all around the year.

Emissions of CH₄ gas at the soil surfaces of the Typic Sulfaquent and the Haplic Sulfaquent were measured following chamber method (chamber was made by acrylic glass with a base of 990 cm² and a content of 27 L) of 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 gases were 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 months of the years.

In order to measure the concentration of CH₄ at the soils and distribution of SO₄ in soil solution, one Typic Sulfaquent and two Haplic Sulfaquent soils from the above mentioned sites (Table I) 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. The SO₄ concentration in the soil solution was determined by the BaCl₂ method after diluting a 50 g of fresh soil in the ratio of 1:1 with distilled water followed by 2 hours of shaking with a mechanical shaker and were analyzed photometrically with the flow injection analyzer (FIA-star 500).

Water content of the initial soil sample was determined (Black, 1965) for the calculation of the detected SO₄ concentration in the soil solution at 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.

The bulk samples obtained from the soils were stored for a couple of days under field conditions (by putting the soil samples into polyethylene bags in an air-tied box) just prior to laboratory analyses, when the sub-samples were air-dried and crushed to 2 mm before analyses. Bulk density, Hydrolic conductivity and Particle size distribution (Day, 1965); Soil pH, Total-N and SO₄²⁻ (Jackson, 1973), Electrical Conductivity from saturation extract of soil (Richards, 1954); organic carbon content (Nelson and Sommers, 1982), Cation exchange capacity (Chapman, 1965), were determined following the procedures as mentioned.

Table I. Selected physical and chemical properties of salt-marsh soils at the Wadden sea coast of Northern Germany

Typic Sulfaquent (Typische Salzhöhmarsh): 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 ⁻¹)	Org.-C (g kg ⁻¹)	Total-N (g kg ⁻¹)	Bulk density (Mg m ⁻³)	Hydrolic con.(cm d ⁻¹)	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	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 ⁻¹)	Org.-C (g kg ⁻¹)	Total-N (g kg ⁻¹)	Bulk density (Mg m ⁻³)	Hydrolic con.(cm d ⁻¹)	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	Water content (%) at different pF values				
	Sand	Silt	Clay	c mol kg ⁻¹	-∞	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 quarterary redox potential of Table II. *ECe = Electrical conductivity of saturation extracts

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 II). The standard deviations (SD) were 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 were varied mostly and the mean values were 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 II). No continuous data were available for the Haplic Sulfaquent-1 (Fig. 1 and 2), and soil was strongly reduced below the upper 0.5 to 1 cm similar (around -100 mV) to that of the Haplic Sulfaquent. The Eh values in the subsoils (50-100 cm) of both the soils indicated that the methanogenesis can be occurred in the soils.

Table II. Mean seasonal 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	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	
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 III. Mean seasonal and calculated annual net emissions of CH₄ from salt-marsh soils in the Wadden sea coast of Northern Germany

Soil unit	Emissions of CH ₄ (μg m ⁻² h ⁻¹)								Emission rates	
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	mg m ⁻² d ⁻¹	g m ⁻² a ⁻¹
Haplic Sulfaquent	-3.36	67	24.9	41	67.7	147	47.1	131	0.82	0.3
Typic Sulfaquent	-5.7	59	8.8	27	18.3	29	-6.2	70	0.09	0.03

Level of Significance:

U-Test	Haplic Sulfaquent			Typic Sulfaquent		
	Spring	Summer	Autumn	Spring	Summer	Autumn
	CH ₄	CH ₄	CH ₄	CH ₄	CH ₄	CH ₄
Summer	2.203**			1.687*		
Autumn	1.137	0.574		2.328**	1.240	
Winter	1.850*	1.957*	0.428	0.231	0.824	1.703*

Level of Significance: 90 % = * and 95 % = **

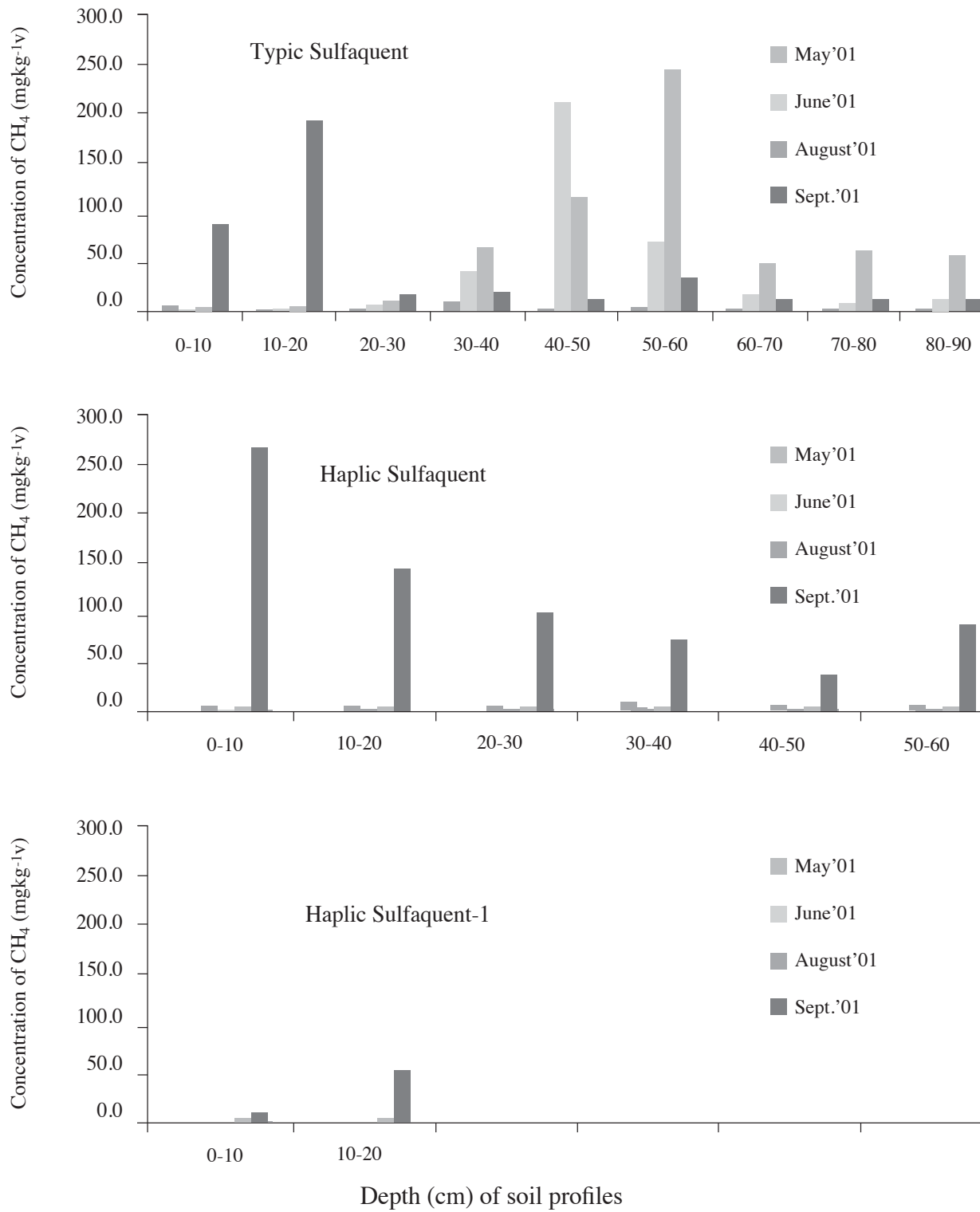


Fig. 1. Concentration of CH₄ throughout the profiles of salt-marsh soils at different times as influenced by the ecosystems of the Wadden sea coast of North Germany

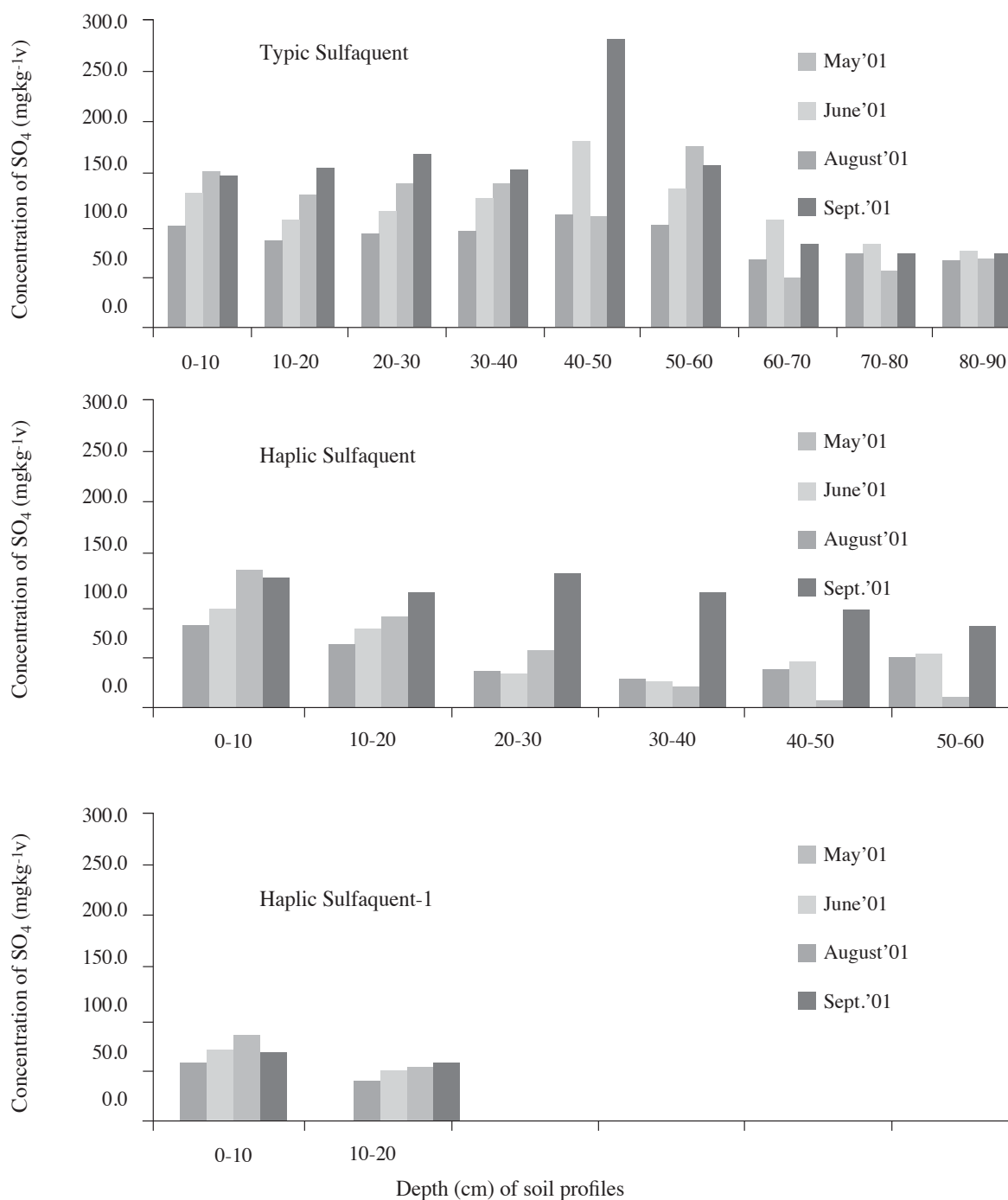


Fig. 2. Distribution of SO₄ throughout the profiles of salt-marsh soils at different times as influenced by the ecosystems of the Wadden sea coast of North Germany

The rH values (Table I) in the epipedon of the Haplic and the Typic sulfaquent were 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. But the rH values in between 13 and 20, where Fe³⁺ can be reduced and FeII/FeIII oxides led to the formation of so called blue green rust, together with reddish brown ferrihydrite

along holes of soil animals and plant roots. In the present study more than 500 mg SO₄ kg⁻¹ were determined in the surface soils of all the profiles in different seasons (Fig. 2), which might be due to the frequent addition of SO₄ from the highly SO₄ enriched sea waters. The rH values of the soils were found to have maintained the established inverse relationships (Schlichting *et al.*, 1995) with the CH₄ productions and/or concentrations and emissions of the soils as reflected by Figs. 1-2 and Table 3. In the subsoils of both the profiles where S/SO₄ should be formed but the present results showed (Fig. 2) a quite reversed trend with the high amount of SO₄ in the surface soils. The formation/concentration of CH₄ in the both the subsoils should not be induced as per rH dynamics (Schlichting *et al.*, 1995), which are also agreed with the present findings (Fig. 1).

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 II) 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. The similar trend of increment of mean annual soil temperature was also observed for wadden soils of the National park in Schleswig-Holstein (Becker, 1998).

Emissions of CH₄

Methane emissions were several folds higher in the Haplic Sulfaquent than that of the Typic Sulfaquent and the annual average emissions of CH₄ were almost 10 folds higher (0.3 g m⁻² a⁻¹) in Haplic Sulfaquent-1 than that (0.03 g m⁻² a⁻¹) of the Typic Sulfaquent (Table III). The relatively small emission also indicates that the CH₄ loss as gas bubbles is restricted to patches covered by water as indicated by the water content of the soils (Table I). Methane emission rates varied seasonally, with the greatest rates in autumn and smallest rates in spring. The small mean efflux in both the soils during summer was probably due to dry weather, which favors oxidation of CH₄ during its movement from the subsoil to the topsoil. Biological

activity was diminished due to low temperature during spring, which results the lowest emissions, while the emissions were increased during summer months of August and September. These increased emissions were not only caused by the higher temperature enhancing more bacterial productivity but also by the high transpiration rate with a direct efflux of CH₄ from the roots to the atmosphere (Sebacher *et al.*, 1985). Holzapfel-Pschorn *et al.* (1987) reported that the 90% of the total emissions of CH₄ from rice field were due to plant transport. Methane oxidation in the soil can be enhanced up to 80% of the total production of CH₄ by methanotropic bacteria (Sass *et al.*, 1990). Cracks in the soil as well as the loss of oxygen in the rhizosphere due to transport of air via aerenchyma enhances the oxidation. The increased rate of CH₄ may be compensated by stronger oxidation in summer and that might be the reason for the moderate variations in emissions of CH₄ between the seasons. The increased emissions of CH₄ during autumn reflects either the increased transpiration rates during these (August-September) months with plant enforced emission of CH₄ or the higher efflux has caused by cracks developed during summer, especially Typic Sulfaquent soil. The cracks have facilitated a quick escape of CH₄ without the possibility of oxidation by bacteria. The seasonal fluctuations of the CH₄ emissions were strongly significant for the Haplic Sulfaquent (Table III). 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. The CH₄ emission rates during spring and winter were negative for Typic Sulfaquent, indicating that there was inconsiderable CH₄ efflux from the wadden and salt marsh soils. Despite of the potentials of CH₄ production according to reduction and content of soil organic matter (Table I), the emissions of CH₄ were low (Table 3). This may be influenced by a strong reduction of sea water SO₄²⁻ makes possible a partly aerobic mineralization of organic matter. Gerrard and Chandon (1993) measured the CH₄ emissions of up to 106 g m⁻² a⁻¹ from peat lands of North Canada. Harris *et al.* (1985) obtained mean emissions of 124 g m⁻² a⁻¹ CH₄. These results are many folds higher than that of the present findings.

Concentrations of CH₄

In Typic Sulfaquent soil, the mean concentrations of CH₄ were measured maximum of 9 mg kg⁻¹ (soil v.) at depths of 30-40 cm followed by 7 mg at depth of 0-10 cm > 5 mg at depth of 50-60 cm during May'01 (Fig. 1). During June'01, the CH₄ concentration was 212 mg at depth of 40-50 cm followed by 71 mg at depths of 50-60 cm > 40 mg at depth of 30-40 cm. The CH₄ concentrations of 245 mg at depth of 50-60 cm > 114 mg at depth of 40-50 cm > 65 mg at 30-40 cm were measured during August'01. The concentrations of CH₄ of 193 mg at depth of 10-20 cm > 87 mg at 0-10 cm > 34 mg kg⁻¹ at 50-60 cm were detected during September'01 (Fig. 1). The sequences of concentrations of CH₄ as measured were August > September

> June > May for Typic Sulfaquent profiles; September > May > August > June for the profiles of Haplic Sulfaquent, and September > August > June for Haplic Sulfaquent-1 profiles. The concentrations of CH₄ at different seasons showed almost inverse relationships with the concentrations of CO₂, indicating the oxidation of CH₄ to CO₂ or vice versa. The average maximum concentrations of CH₄ in the soils of each of the above mentioned section of the cylinder were measured during August'01 (68 mg kg⁻¹ v.) followed by September'01 (45 mg) > June'96 (41 mg) > May'01 (4 mg) for the Typic Sulfaquent soils and September'01 (250 mg) > May'01 (6 mg) > August'01 (4 mg) > June'01 (3 mg kg⁻¹ v.) for the profiles of Haplic Sulfaquent. The Haplic Sulfaquent-1 showed almost similar pattern of distribution of concentrations of CH₄ in the profiles, except for the August'01, which ranked second highest position in the order of seasonal measurements. In all the profiles, the concentrations of CH₄ were very low, which was due to the results of oxidation of CH₄ as well as the high amount of SO₄ contents in the soils (Fig. 2). The SO₄ content in the soils might have prevented the methanogenesis. The concentrations of CH₄ were significantly (p≥0.05) varied with the seasons as well as with the depths. The concentrations of CH₄ showed no dependence to temperature.

High temporal and spatial variations in CH₄ emissions led to question whether the emission pattern reflects the concentration of this gas in the soil. The highest concentrations at each sampling times (up to 245 mg CH₄ kg⁻¹ soil v.) were found in the Typic Sulfaquent soil and the lowest concentrations were in the Haplic Sulfaquent soils, which were almost in the range of atmospheric concentration (1.65 mg CH₄ kg⁻¹ v.). Stratification, aggregation and/or variable pore volume with different continuity may lead to an inhomogeneous soil with the formation of traps where produced CH₄ 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 Haplic Sulfaquents have comparatively high 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 CH₄ loaded water upward without exporting the soil solution from the system as the hydraulic conductivity of 68 to 96 cm d⁻¹ in the upper soil which is much lower than the rising tide, leading to an enclosure of the entrapped soil solution. The SO₄ concentrations in the studied soil solutions were a few folds higher (Fig. 2) than that of the sea water indicating a low exchange rate between the soil solutions and marine water. But the finding differed with the results of Giani *et al.* (1996) who reported that the sulfate concentration was lower than sea water.

Methane oxidation mediated mainly by methanotrophic bacteria is the responsible process, which is strongly inhibited by ammonium accessible for nitrification (Hütsch, 2001).

Indeed, in many studies NH₄ was identified as a strong inhibitor for CH₄ oxidation (Bronson and Mosier, 1994; Hütsch, 1998). Root derived organic C can contribute to various C pools and become an origin of CH₄ emitted from flooded soils (Lu *et al.*, 2000). In the total amount of atmospheric CH₄, the contribution of CH₄ from sulfate-rich soils is negligible, because sulfate-reducing and methane producing organisms complete for the same substrates (H₂/CO₂, acetate-competitive substrates) but the sulfate reducers have the competitive advantage: they have stronger affinity to the competitive substrates and can use them to provide more energy than the methane producers (Schönheit *et al.*, 1982). Increasing methane and decreasing sulfate concentrations (methane-sulfate transition) are found in some deeper depths, but not consistent with the seasons. Most of the soils contained more CH₄ in August-September than those of May-June, indicating no methane-sulfate transition, which means sulfate reduction is not limited and methanogenesis is suppressed down to that depth. As methanogenesis is strictly anaerobic, more CH₄ was expected in the more anaerobic soils. However, this was not proved by this study. The soils under more anaerobic condition (near the sea) did not contain maximum methane nor did the more aerobic soil (far away from the sea) contain the least. This suggesting that there seemed to be no relation between methane concentration and degree of soil development. There was also no evident relation between the redox properties and their corresponding methane concentrations.

Distribution of SO₄

Generally there should be noticeable SO₄ contents in the surface soils of both the profiles only if we look for the colour (Table I) and redox (Table II) of the soils. Whereas in the subsoils, sulfates should be reduced to sulfide. But the realities, SO₄ were determined in the subsoils of all the profiles in different seasons, where the sulfate concentrations in the soil solutions were higher in all the seasons at depths of 50-60 cm followed by surface soils of Typic sulfaquent (Fig. 2). In both the profiles of Haplic Sulfaquent, the maximum amounts of SO₄ in the soil solutions were detected in the surface soils and decreased towards the deeper depths, except for the depth of 20-30 cm where the maximum content of SO₄ was determined in the profile of Haplic Sulfaquent during September'01 (Fig. 2). The maximum average concentrations of SO₄ throughout the profiles of Typic Sulfaquent and Haplic Sulfaquent were determined during September'01, while the minimum average concentrations of SO₄ were obtained from all the profiles during May'01. The SO₄ contents were observed maximum in the Typic Sulfaquent followed by Haplic Sulfaquent during all the seasons, except for the September'01 (Fig. 2). The high concentration of SO₄ was thought to be the result of the frequent intrusion of highly SO₄ (> 600 mg SO₄ L⁻¹) enriched sea waters.

The concentrations of SO_4 throughout the profiles of all the soils were quite inversely distributed in relation to CH_4 concentrations round the year, except for the depths of 40-50 cm during June'01 and 50-60 cm during August'01 for the Typic Sulfaquent profile where both the CH_4 and SO_4 contents were high. These indicate that there may be a coexistence of sulfate reducing and methane producing bacteria as reported by Holmer and Kristensen (1994). Schipper and Reddy (1994) also measured high CH_4 concentration despite of the higher sulfate concentration in the soil solution. The presence of SO_4 in the soil solution is thought to be incompatible with CH_4 production as SO_4 is supposed to be toxic to methanogenesis at a level of 320 mg $\text{SO}_4 \text{ L}^{-1}$ (Jacobsen *et. al.*, 1981). King (1988) regards the concentration level of 32 mg $\text{SO}_4 \text{ L}^{-1}$ as critical; high concentration of SO_4 in the soil and CH_4 production should therefore be contrary (Rehburgh and Heggie, 1977). In this study, the SO_4 concentration in the soil solution was at least the concentration of sea water (600 mg $\text{SO}_4 \text{ L}^{-1}$) and in some depths which were above the claimed toxic level. Although it was thought that at deeper depths, the SO_4 concentration should be lower due to SO_3 , but there was only a little decreasing tendency of SO_4 concentration towards the deeper depths. There is no noticeable correlation ($r = -0.09$) was obtained between the SO_4 and CH_4 concentrations. Moreover, even CH_4 was determined at depths where the SO_4 concentration in the soil solution was around 1200 mg $\text{SO}_4 \text{ L}^{-1}$. This indicates that either CH_4 production is compatible even with the higher SO_4 concentration.

Conclusion

The present study concludes that the CH_4 fluxes varied significantly among the seasons, which also evident that for certain periods of the year the coastal salt marsh soils can act either as a sink or source for atmospheric CH_4 depending on the physical and chemical properties of the soils. The methane emission was low resulting from low formation of CH_4 which was due to a high SO_4 in put from SO_4 enriched sea water together with an oxidation of CH_4 during the upward movement of CH_4 from the subsoil to the atmosphere. There was also no significant concentration/efflux of CH_4 , suggesting almost no contribution to atmospheric methane. The heterogeneity in redox potential of the soils studied also indicate that CH_4 oxidation is likely to take place, and the CH_4 emission and concentration gradients suggest that the CH_4 produced is readily oxidized within the soils. Further research should be focused on more detailed look on the geophysical conditions of the soils regarding unpredictable concentrations and emissions of trace gases. The determination of CH_4 oxidation and SO_4 reduction rates are also necessary.

References

- Becker G (1998), Wassertemperatur *In: Umwelt atlas Wattenmeer*, Eds. Kohlus J and Küpper H, E. Ulmer, Stuttgart, pp 62-63.
- Black CA (1965) Methods of Soil Analysis, Part 2, Series 9, Am Soc. Agron. Inst. Publ., Madison, WI, USA, pp. 894-1372
- Bronson KF and Mosier AR (1994), Suppression of methane oxidation in aerobic soil by nitrogen fertilizers, nitrification inhibitors, and urease inhibitors, *Biol. Fertile. Soils*. **17**: 263-268.
- Chapman HD (1965), Cation exchange capacity *In: Methods of Soil Analysis-II*, Agron. Series 9, Ed. Black CA, Am. Soc. Agron. Publ., Madison, WI, USA, pp 891-900.
- Conrad R (1989), Control of methane production in terrestrial ecosystems *In: Exchange of trace gases between terrestrial ecosystems and the atmosphere*, Eds. Andreae MO and Schimmel DS, J. Wiley and Sons Publisher, pp 39-58.
- Day PR (1965), Particle fractionation and particle size analysis *In: Methods of Soil Analysis*, Part 2, Agron. Series 9, Ed. Black CA, Am. Soc. Agron. Publ., Madison, WI, USA, pp 545-566.
- Duxbury JM (1995), The significance of agricultural sources of greenhouse gas emissions from soil of tropical agroecosystems *In: Soil management and greenhouse effect*, Ed. Lal R, Lewis Publ., Boca Raton, FL, USA, pp 179-291.
- Gerrard G and Chandon J (1993), Quantification of methane oxidation in the rhizosphere of emergent aquatic macrophytes: defining upper limits, *Biochemistry* **23**: 79-97.
- Giani L, Ditttrick K, Martsfeld-Hartmann A and Peters G (1996), Methanogenesis in salt marsh soils of the North Sea Coast of Germany, *Europ. J. of Soil Sci.* **47**: 175-182.
- Ghosh A, Patra PK, Ishijima K, Umezawa T, Ito A, Etheridge DM, Sugawara S, Kawamura K, Miller JB, Dlugokencky EJ, Krummel PB, Fraser PJ, Steele LP, Langenfelds RL, Trudinger CM, White JWC, Vaughn B, Saeki T, Aoki S and Nakazawa T (2015), Variations in global methane sources and sinks during 1910–2010, *Atmos. Chem. Phys.* **15**(5): 2595–2612. doi:10.5194/acp-15-2595-2015.
- Harris RC, Gorham E, Sebacher DI, Bartlett KB and Flebbe PA (1985), Methane flux from Northern peatland, *Nature* **315**: 652-653.
- Holmer M and Kristensen E (1994), Coexistence of sulfate

- reduction and methane production in an organic-rich sediment, *Marine Ecology* **107**: 177-184.
- Holzappel-Pschorn A, Conrad R and Seiler W (1987), Effects of vegetation on the emission of methane from submerged paddy soil, *Plant and Soil* **92**: 223-233.
- Hou AX, Chen GX, Wang ZP, Van Cleemput O and Patrick Jr., WH (2000), Methane and nitrous oxide emissions from a rice field in relation to soil redox and microbiological processes, *Soil Sci. Soc. Am. J.* **64**: 2180-2186.
- Hütsch BW (1998), Methane oxidation in arable soil as inhibited by ammonium, nitrate, and organic manure with respect to soil pH, *Biol. Fertil. Soils* **28**: 27-35.
- Hütsch BW (2001), Methane oxidation, nitrification, and counts of methanotrophic bacteria in soils from a long-term fertilization experiment ("Ewiger Roggenbau" at Halle), *J. Plant Nutr. Soil Sci.* **164**: 21-28.
- IPCC (Intergovernmental Panel on Climate Change) (2013), Climate Change 2013: The Physical Science basis, Working Group I Contribution to the Fifth Assessment Report of the IPCC, Cambridge University Press, New York.
- Hutchinson GL and Misier AR (1981), Improved soil cover method for field measurement of nitrous oxide fluxes, *Soil Sci. Soc. Am. J.* **45**: 311-316.
- Jackson ML (1973), Soil Chemical Analysis, Prentice Hall of India Pvt. Ltd., New Delhi.
- Jacobsen P, Patrick WH and Williams BG (1981), Sulfide and methane formation in soils and sediments, *Soil Sci.* **132**: 279-287.
- King G M and Wiebe W J 1978: Methane release from soils of a Georgia salt marsh, *Geochim. Cosmochim. Acta.* **42**: 343-348.
- King GM (1988), Patterns of sulphate reduction and sulphur cycle in a South Carolina salt marsh, *Limnology and Oceanography* **33**: 376-390.
- Lu Y, Wassmann R, Neue HU and Huang C (2000), Dynamics of dissolved organic carbon and methane emissions in a flooded rice soil, *Soil Sci. Soc. Am. J.* **64**: 2011-2015.
- Meng L, Paudel R, Hess PGM and Mahowald NM (2015), Seasonal and interannual variability in wetland methane emissions simulated by CLM4Me' and CAM-chem and comparisons to observations of concentrations, *Biogeosciences* **12(13)**: 4029-4049, doi:10.5194/bg-12-4029-2015.
- Nelson DW and Sommers LE (1982), Total carbon, organic carbon and organic matter *In*: Methods of Soil Analysis, Part 2, Agron. Series 9, Ed. Page AL, Am. Soc. Agron. Publ., Madison, WI, USA, pp 539-579
- Rehburgh WS and Heggie DT (1977), Microbial methane consumption reactions and their effects on methane distribution in freshwater and marine environments, *Limnology and Oceanography* **22**: 1-9.
- Richards LA ed. (1954), Diagnosis and improvement of saline and alkali soils *In*: USDA Handbook No. 60. US Govt. Print. Office, Washington, USA, pp 84-156.
- Sass RL, Fisher FM, Harcombe PA and Turner FT (1990), Methane production and emission from a Texas rice field, *Global Biochem. Cycles* **4**: 47-68.
- Schipper LA and Reddy KR (1994), Methane production and emissions from four reclaimed and pristine wetlands of Southern United States, *Soil Sci. Soc. Am. J.* **58**: 1270-1275.
- Schlichting E, Blume H-P and Stahr K (1995), Boden-Kundliches Praktikum, 2. neubearbeitete Auflage, Blackwell Wissenschafts-Verlag Berlin.
- Schönheit P, Kristjansson JK and Thauer RK (1982), Kinetic mechanism for the ability of sulfate reducers to out-compete methanogens for acetate, *Archives of Microbiology* **132**: 285-288.
- Sebacher DI, Harris RC and Bartlett KB (1985), Methane emissions to the atmosphere through aquatic plants, *J. Environ. Qual.* **14**: 40-46.
- Spahni R, Wania R, Neef L, van Weele M, Pison I, Bousquet P, Frankenberg C, Foster PN, Joos F, Prentice IC and van Velthoven P (2011), Constraining global methane emissions and uptake by ecosystems, *Biogeosciences* **8(6)**: 1643-1665.
- Takai Y and Wada E (1990), Methane formation in waterlogged paddy soils and its controlling factors *In*: Soils on warmer earth-Development in Soil Science 20, Eds. Scharpenseel HW, Schomaker M and Ayoub A, Elsevier, Amsterdam, pp 101-107.
- Voulgarakis A, van Weele M, Weiss RF, Williams JE and Zeng G (2013), Three decades of global methane sources and sinks, *Nature Geosci.* **6(10)**: 813-823.

Received: 11 December 2016; Revised: 22 January 2017;
Accepted: 29 May 2017.