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# Emissions of Porewater Compounds and Gases from the Subaquatic Sediment Disposal Site “Rodewischhafen”, Hamburg Harbour

## Abstract

In the year 1993 a confined and unused harbour basin was used to store 300,000 m<sup>3</sup> of fine-grained dredged material from Hamburg Harbour. About 70% of the deposit surface was covered with water. Only the rim areas were above the water level and covered with reed. Emissions of dissolved compounds into the groundwater, as well as surface emissions of methane and carbon dioxide were measured between 1994-1997. As indicators for the water fluxes from the deposit area we used NH<sub>4</sub><sup>+</sup> and HCO<sub>3</sub><sup>-</sup> because of their high concentrations in sludge porewater in comparison to groundwater. The average concentrations of NH<sub>4</sub><sup>+</sup> and HCO<sub>3</sub><sup>-</sup> in the porewater increased during two years

from 85 to 250 mg NH<sub>4</sub><sup>+</sup> l<sup>-1</sup> and from 1.6 to 2.1 g HCO<sub>3</sub><sup>-</sup> l<sup>-1</sup>. In contrast, the groundwater from different sample sites around the deposit in 4-9 m depth showed constant concentrations of about 8 mg NH<sub>4</sub><sup>+</sup> l<sup>-1</sup> and 0.7 g HCO<sub>3</sub><sup>-</sup> l<sup>-1</sup>. Furthermore, the average gas emissions over the water surface were 3.5 g CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> and 1.2 g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>. The land surface emission of CO<sub>2</sub> showed with 1.1 g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> similar emission rates, but almost no methane was released from land areas. The results indicated, that there were no significant emissions of porewater compounds from the subaquatic sediment deposit into the groundwater, but there was a high emission of the greenhouse gas CH<sub>4</sub> over the water surface into the atmosphere. This paper was first presented in September 1997 at the ICCS, Rotterdam, The Netherlands, and was published in the conference proceedings. This revised version is reprinted here with permission.



Figure 1. Aerial view of the “Rodewischhafen” with the surrounding harbour facilities. At the time, the dam of the “Rodewischhafen” was constructed but no sludge was as yet pumped in.

## Introduction

A confined and unused harbour basin with a surface area of 42,000 m<sup>2</sup> was used to store 300,000 m<sup>3</sup> of fine-grained dredged material from Hamburg Harbour below the water table. The harbour sludge is polluted mainly by heavy metals and arsenic and is characterised by high concentrations of organic material between 3 and 7% TOC. The decay of carbon leads to anaerobic conditions and thus to gas production in the sludge deposit. Existing gas inclusions as well as a high content of clay and silt (50-98%) result in a low water permeability of the sludge. Production and emission rates of the greenhouse gases methane and carbon dioxide were determined. High CH<sub>4</sub>-emissions may cause explosive gas mixtures (5-15% CH<sub>4</sub> in at least 11.6 % O<sub>2</sub>, Rettenberger 1994) in confined areas. This could be the case, if the deposit area would be used for construction purposes. The aim of the investigation was to find out, if the sludge deposit contributes under subaquatic storage conditions to the groundwater pollution and to the emissions of greenhouse gases.

## SITE DESCRIPTION AND METHODS

Photographs of the harbour and of the harbour sediment deposit "Rodewischhafen" are shown in Figures 1 and 2. The large water surface with an average water depth of 30 cm, as well as the reed covered rim, which was up to 50 cm above the water table is visible. Figure 3 shows a sketch of the deposit with surrounding sand and low permeable estuarine loamy clay layers. The sludge was stored mainly subaquatic. About 30% of the area had a land surface which was covered with reed. The average depth of the deposit was 7 m below the water table. Throughout the year the water table changed about  $\pm 5$  cm. The groundwater flow in this harbour region was from north to south, therefore we used the monitoring well RM2 to measure porewater emissions into the groundwater layers A and B. The groundwater layer B had a broad distribution and was influenced by the tide, whereas layer A was only locally distributed and showed almost stagnant conditions. At the down-gradient position RM2 a conventional monitoring well with 20 m screen length (10-30 m below water table) was used to collect groundwater samples from layer B by pumping. In layer A a multi-tube well with three monitoring points (3 to 5 m below water table) was installed, the samples were collected by a vacuum pump device.

### Sampling techniques

*Porewater samples.* Porewater samples (50 ml) were collected with suction lysimeters, permanently installed at depth of 3, 4 and 5 m below water table. To avoid precipitation of cations or phosphates, the collection bottles were pre-filled with 1 ml  $\text{HNO}_3$  (32%) or 2 ml  $\text{H}_2\text{SO}_4$  (38%), respectively. For other anions and ammonium no pre-filling was carried out. The chemical parameters were analysed afterwards in the laboratory.

### Chemical and physical analyses

*Measurement of ground- and porewater compounds.* The chemical composition of the water samples were



Figure 2. Close up of the subaquatic harbour sediment deposit at the "Rodewischhafen", Hamburg.



Martin Kussmaul, winner of the IADC Award, shown with Mr Hans van Diepe, Chairman of the IADC Editorial Board, at the International Conference on Contaminated Sediments, Rotterdam.

## IADC Award 1997

**Presented during the International Conference on Contaminated Sediments, Rotterdam, The Netherlands September 7-11, 1997**

At the International Conference on Contaminated Sediments, held in Rotterdam from September 7-11, 1997, Dr Martin Kussmaul was presented with the annual IADC Award for younger authors.

Dr Kussmaul graduated in 1991 from the University of Konstanz, Germany with a degree in Hydrology. He then moved to the University of Hamburg where in 1994 he received a PhD in microbial ecology. Since 1995 he has been employed at the Institute of Soil Science at the University of Hamburg, where he produced this paper with his colleague at the institute, Alexander Groengroeft, and Dr Harald Koethe of the Federal Institute of Hydrology, Koblenz, Germany. Each year at a selected conference, the International Association of Dredging Companies grants an award to a paper written by a young author. The paper Committee of the conference is asked to recommend an author who is younger than 35 years of age and whose paper makes a significant contribution to the literature on dredging and related fields. The purpose of the award is "to stimulate the promotion of new ideas and encourage younger men and women in the dredging industry". The IADC Award consists of US\$1,000, a certificate of recognition and publication in *Terra et Aqua*.

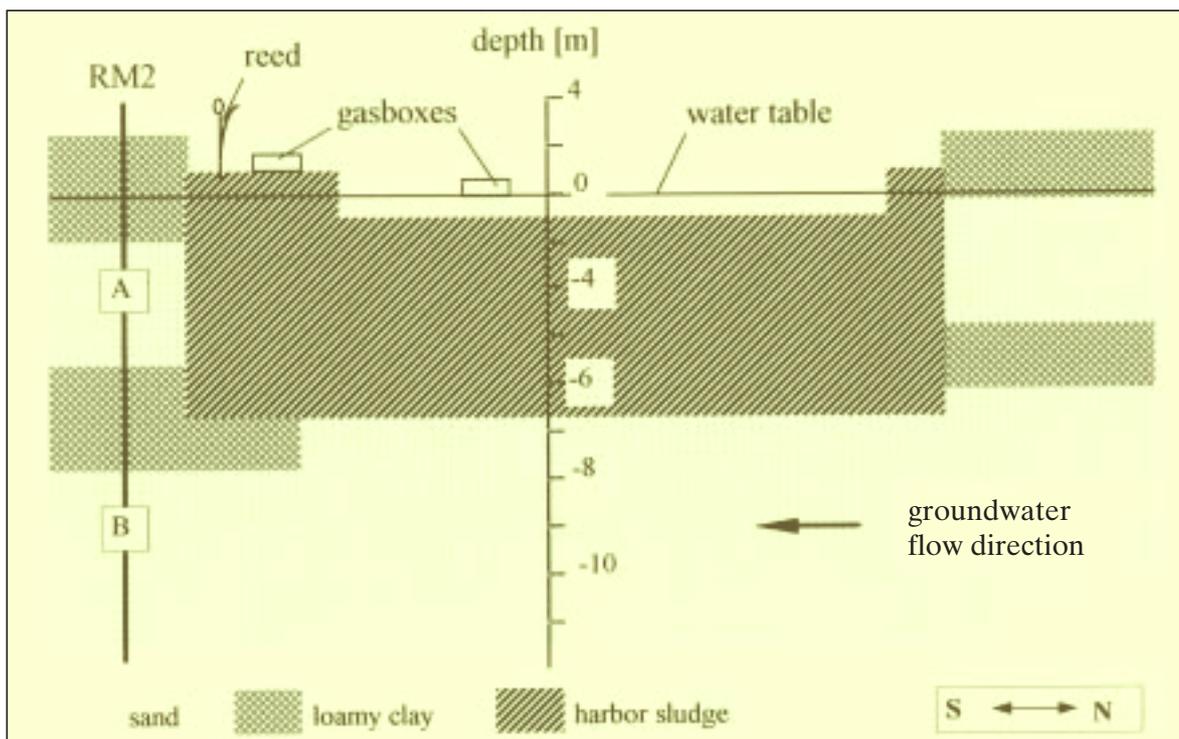


Figure 3. Sketch of the subaquatic harbour sludge deposit "Rodewischhafen" with groundwater sampling site RM2-A/B and the gasbox locations. The deposit contained 300,000 m<sup>3</sup> sludge with a surface area of 42,000 m<sup>2</sup>.

determined by using standard analytical procedures: titration (HCO<sub>3</sub><sup>-</sup>), anionchromatography (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>), photometry (NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>2-</sup>), AES (Na<sup>+</sup>, K<sup>+</sup>) and AAS (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, As).

#### Gas analyses

The concentrations of methane, carbon dioxide and oxygen were measured with a gaschromatograph (Fisons GC 6000). A flame ionisation detector (FID) was used to determine low concentrations of methane (< 0.5%). Higher CH<sub>4</sub>-concentrations as well as O<sub>2</sub> and CO<sub>2</sub> were detected by a hot wire detector (WLD). The variation of the measurement was 2% for CH<sub>4</sub> and CO<sub>2</sub> and 5% for O<sub>2</sub>.

#### Gas production and gas emission

##### Gas production

Sludge cores were taken with a beaker sampler out of the center of the deposit in 0 to 4 m depth. A gastight 130 ml flask with rubber septum was filled with 80 ml of sludge from different depth and immediately flushed with nitrogen. The increase of CH<sub>4</sub> and CO<sub>2</sub> in the headspace was measured after 12 h of incubation for the following 48 h. During that time the samples were incubated at the corresponding depth temperature of the deposit in the dark. Afterwards the flask was refilled with water. The weight of the added water corresponds to the gas volume in the bottle. Gas production rates were calculated by a linear regression in [g m<sup>-3</sup> fw sludge d<sup>-1</sup>].

##### Gas emission

Gasboxes were used to determine the gas emissions over the water and land surface (Figure 4). The increase

Table I. Average porewater concentrations of anions, cations and trace metals from 1994 to 1996.

anions [mg l <sup>-1</sup> ]		cations [mg l <sup>-1</sup> ]		heavy metals and As [mg l <sup>-1</sup> ]	
Cl <sup>-</sup>	40	NH <sub>4</sub> <sup>+</sup>	189	Zn <sup>2+</sup>	16.5
SO <sub>4</sub> <sup>2-</sup>	n.d.	Na <sup>+</sup>	107	Cd <sup>2+</sup>	< 0.1
NO <sub>3</sub> <sup>-</sup>	n.d.	K <sup>+</sup>	35	Cu <sup>2+</sup>	1.2
PO <sub>4</sub> <sup>2-</sup>	1.4	Mg <sup>2+</sup>	71	Cr <sup>3+</sup>	4.7
HCO <sub>3</sub> <sup>-</sup>	1810	Ca <sup>2+</sup>	428	Ni <sup>2+</sup>	4.5
measured					
HCO <sub>3</sub> <sup>-</sup>	2470	Fe <sup>2+</sup>	64	Pb <sup>2+</sup>	< 3.0
calculated					
		Mn <sup>2+</sup>	16	As	6.2

n.d. = not detectable.

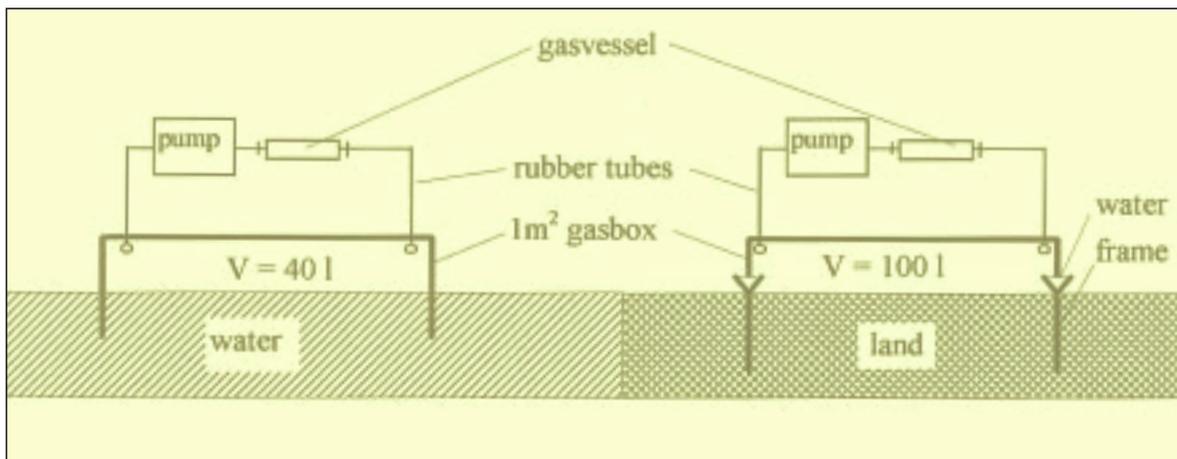


Figure 4. Gasboxes to determine gas emissions over the water and land surface.

of CH<sub>4</sub> and CO<sub>2</sub> in the box was measured for 6 h. Every 45 min a gas vessel was replaced and afterwards analysed in the laboratory. Gas emission rates were calculated by linear regression in [g m<sup>-3</sup> fw sludge d<sup>-1</sup>].

(carbonate buffering, cation exchange) the concentrations of HCO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> have been significantly (*P* < 0.05) increased from the beginning of the investigation. From regression analysis on

RESULTS AND DISCUSSION

Chemical parameters of the ground- and porewater

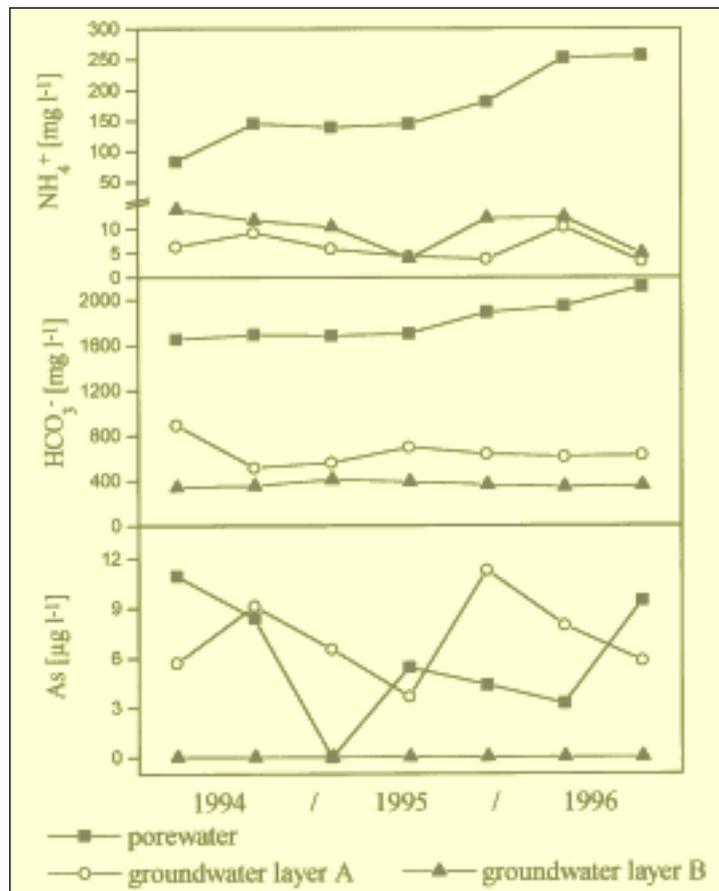
Table I shows the porewater composition as median values over time (Oct. 1994 to Sept. 1996) and sample depth (1-5 m below deposit surface). Owing to the high TOC of the harbour sludge and the absence of oxygen, nitrate and sulfate have been totally reduced. The concentration of chloride is still in the range of the water from the River Elbe, which was primarily used for flushing the dredged material in the harbour basin.

The main anionic constituent of the porewater is hydrocarbonate (90 % of the sum of anions). Part of the HCO<sub>3</sub><sup>-</sup> is lost owing to the sampling technique (precipitation in the lysimeter tubes as Ca- or Fe-carbonates, gaseous loss as CO<sub>2</sub>), therefore the concentration of HCO<sub>3</sub><sup>-</sup> was calculated from ion balance.

The concentration of ammonium was high, single values varied between 66 and 300 mg l<sup>-1</sup>. Phosphate behaves irregular, partly not being detectable, partly showing considerable concentrations up to 10 mg l<sup>-1</sup>. Potassium, magnesium and calcium have been markedly increased in comparison to the Elbe water, whereas the content of sodium was still in the range of riverine water. The low redox potentials of the sediments resulted in increased concentrations of mobile iron and manganese. The concentrations of heavy metals were low, only the solubility of arsene had to be considered.

Vertical differences in the porewater composition were rather small. Owing to the mineralisation of organic material and subsequent geochemical processes

Figure 5. NH<sub>4</sub><sup>+</sup>, measured HCO<sub>3</sub><sup>-</sup> and As-concentrations in the ground- and porewater from 1994 to 1996. The data of porewater and groundwater layer A are the mean value of three replicates, whereas each data point of layer B represents one single measurement.



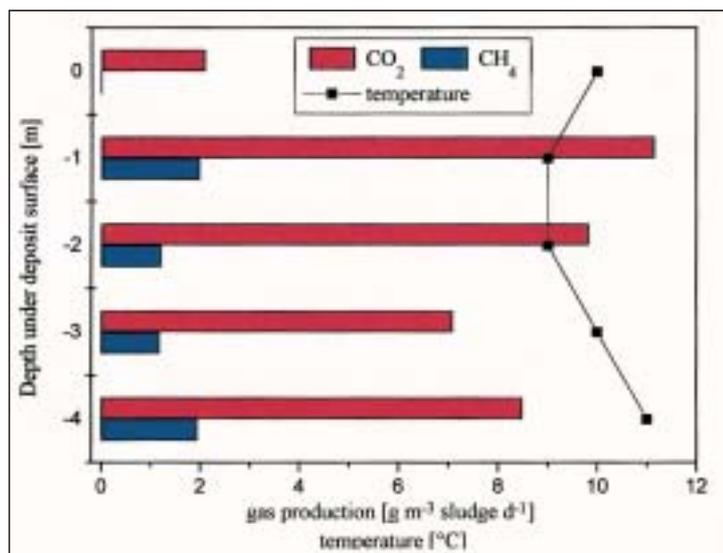


Figure 6. Gas production rates of the fresh sludge with the corresponding depth temperatures from 24. April 1996.

all individual values ( $n = 32$  to  $40$ ) the mean annual increase was calculated for  $\text{HCO}_3^-$  with  $9.40$ ,  $\text{NH}_4^+$ :  $4.66$ ,  $\text{Na}^+$ :  $0.50$ ,  $\text{K}^+$ :  $0.15$ ,  $\text{Mg}^{2+}$ :  $0.37$  and  $\text{Ca}^{2+}$ :  $1.47$  (values in  $\text{mmol l}^{-1} \text{a}^{-1}$ ). These calculated trends were nearly charge balanced (anions  $+9.40 \text{ mmol}_{\text{eq}} \text{l}^{-1} \text{a}^{-1}$ , cations  $+9.00 \text{ mmol}_{\text{eq}} \text{l}^{-1} \text{a}^{-1}$ ).

From the measured change in porewater composition it was possible to calculate the potential release of gaseous C from mineralisation on a unit area. Using a water content of 70% fresh weight, a particle density of  $\rho = 2.55 \text{ g cm}^{-3}$ , a depth of the disposed sludge of  $h = 6 \text{ m}$  and an organic carbon content of 4.1 % the unit area consisted of  $2.2 \text{ t dry matter m}^{-2}$  and  $5.1 \text{ m}^3$  porewater  $\text{m}^{-2}$  with the dry matter containing  $90 \text{ kg organic carbon m}^{-2}$ .

Using two different C/N-ratios (C/N-ratio measured =  $10.5 \text{ mol mol}^{-1}$ , C/N-ratio according to Redfield =  $6.625 \text{ mol mol}^{-1}$ ) the measured increase in ammonium content in pore water ( $4.66 \text{ mmol l}^{-1} \text{a}^{-1}$ ) results in a net-C-mineralisation of  $3.0 \text{ kg C m}^{-2} \text{a}^{-1}$  or  $1.9 \text{ kg C m}^{-2} \text{a}^{-1}$ . Part of the mineralised carbon leads to an increase in alkalinity ( $9.4 \text{ mmol l}^{-1} \text{a}^{-1}$ ), thus the potential release of gaseous C has to be reduced to  $2.4 \text{ kg C m}^{-2} \text{a}^{-1}$  or  $1.3 \text{ kg C m}^{-2} \text{a}^{-1}$ .

These calculations showed, that the daily rates of C-mineralisation may vary between  $3.7$  and  $6.7 \text{ g C m}^{-2} \text{d}^{-1}$ . It is yet not considered, which part of the mineralised N is adsorbed as  $\text{NH}_4^+$ -cation by matrix (leading to an increase in calculated C-mineralisation) and to which content the increase in alkalinity is caused by carbonate buffering thus not decreasing the mineralised C. The influence of the subaquatic disposal on adjacent groundwater layers should be easily detectable by a change in bicarbonate or ammonium content. As shown above, these parameters are high concentrated in the

sediment porewater, whereas the background values of typical Elbe river concentrations are low ( $\text{HCO}_3^-$ :  $338 \text{ mg l}^{-1}$ ,  $\text{NH}_4^+$ :  $8.7 \text{ mg l}^{-1}$ , Groengroeft and Miehlisch, 1995).

Figure 5 shows the concentrations of these indicator parameters in groundwater layer A and B. The concentrations varied slightly with time but were still in the low range of bank infiltrated water. In layer A the quality was worse than in layer B, as illustrated by arsenic, but the compositions of anions and cations indicated, that there was no direct response on the sludge disposal. Thus it could be concluded, that the influence of subaquatic disposal on groundwater quality was lacking or rather small. This result corresponded with the low permeability of the disposed sludge and the observed termination of the consolidation process (Schwieger, personal comm.).

### Gas production and gas emissions

Gas production rates of the sludge deposit from different depth are shown in Figure 6. Methane production varied between  $0$  and  $2 \text{ g CH}_4 \text{ m}^{-3} \text{ fw sludge d}^{-1}$ . No  $\text{CH}_4$  was formed in the upper oxic layer of the deposit. However, the  $\text{CH}_4$ -production corresponds to the course of the temperature profile. In contrast, the  $\text{CO}_2$ -production ranged between  $2$  and  $11 \text{ g CO}_2 \text{ m}^{-3} \text{ fw sludge d}^{-1}$ . The lowest  $\text{CO}_2$ -production occurred in the upper deposit layer. The anoxic decay of carbon in deeper sludge layers led obviously to a higher  $\text{CO}_2$ -formation.

### Methane

The release of methane and carbon dioxide into the atmosphere over the water and land surface is shown in Figure 6. Extremely high methane emissions between  $0.2$  and  $7 \text{ g m}^{-2} \text{d}^{-1}$  were measured over the water surface. The highest  $\text{CH}_4$ -emission was observed in summer. But also winter emissions rates showed high values. This indicated, that the gas emission was not only dependent on temperature but also on the atmospheric pressure or for example algae blooms in April. In summer, the methane release occurred mainly in form of gas bubbles coming out of the sludge. Therefore, the resting time of methane in oxic sludge and water layers was too short for an effective reduction of methane by methanotrophic bacteria. On the other hand, almost no significant  $\text{CH}_4$ -emission could be observed over the land surface. There was obviously a very effective methane oxidising bacterial community in the sludge layer above the water table, which was able to oxidise the methane coming from deeper layers. In comparison, natural Elbe marshland show much lower  $\text{CH}_4$ -emissions of  $0 - 0.05 \text{ g CH}_4 \text{ m}^{-2} \text{d}^{-1}$  (Pfeiffer, 1994).

### Carbon dioxide

The emissions of carbon dioxide over the water and land surface varied between  $0$  and  $4.5 \text{ g m}^{-2} \text{d}^{-1}$

throughout the year (Figure 7). But the land emissions showed more temperature dependent emission rates with highest values in summer and lowest in winter. However, the land  $\text{CO}_2$ -emissions were in the range of natural marshland emissions of  $1.1 - 5.5 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$  (Nyman and DeLaune, 1991). Only a small part of the produced  $\text{CO}_2$  (see Figure 6) was emitted over the surface areas. Reasons were the good solubility of  $\text{CO}_2$  in water and its chemical reactions with ions and surfaces. Additionally,  $\text{CO}_2$  is fixed by autotrophic bacteria and plants for growth.

In total, the average gas surface emissions of the entire sludge deposit Rodewischhafen were approximately  $140 \text{ m}^3 \text{ CH}_4 \text{ d}^{-1}$  and  $26 \text{ m}^3 \text{ CO}_2 \text{ d}^{-1}$ . However, these gas emissions were low compared to landfills of the same size (Ehrig 1994).

## Conclusions

The subaquatic deposition of dredged material offers a good opportunity to store contaminated harbour sediments. No emission of contaminants into the groundwater could be observed in this case, mainly because of the low water permeability of the sludge. The concept of subaquatic disposal, as proposed by Bertsch and Knoepp (1990), can be supported with this data. The high emissions of the greenhouse gas methane over the water surface can be reduced by an oxic soil layer, which covers the deposit above the water table. The use of a plant cover promotes aeration of the upper soil and binds  $\text{CO}_2$ .

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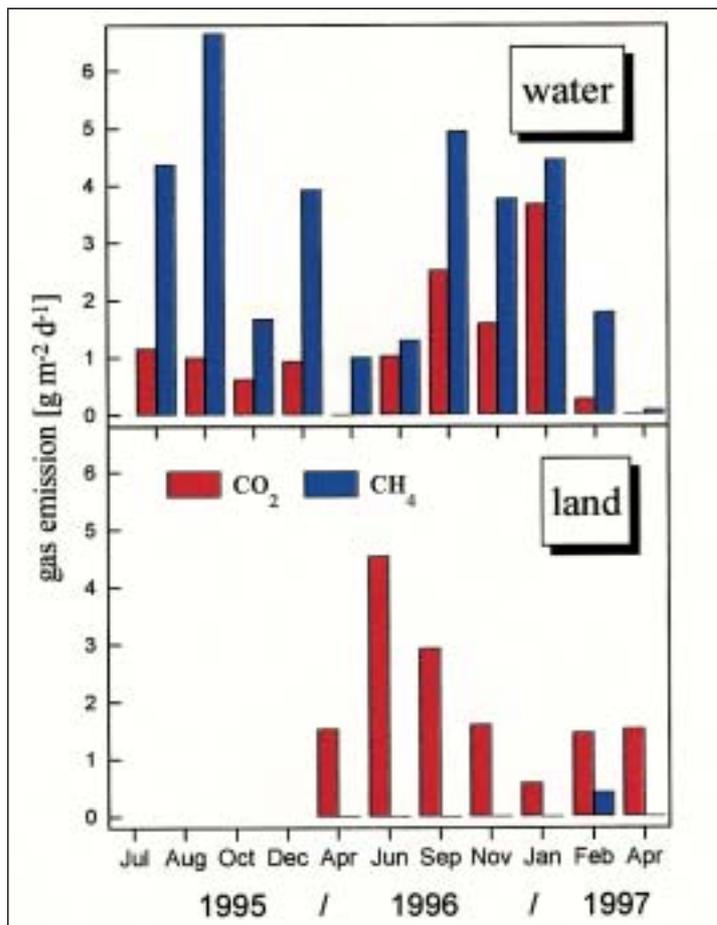


Figure 7. Gas emissions over the water and land surface of the sludge deposit “Rodewischhafen” from 1995 to 1997.

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