

## Mitigation of methane emissions from constructed wetlands

S R Pangala<sup>1</sup>, D S Reay<sup>2</sup> and K V Heal<sup>1</sup>

<sup>1</sup>School of Geosciences, University of Edinburgh, Edinburgh EH9 3JN, UK

<sup>2</sup>School of Geosciences, University of Edinburgh, EH8 9XP, Edinburgh, UK

### Abstract

Wetlands are increasingly being used as a sustainable solution to treat water pollution problem worldwide and are also the single largest source of the powerful greenhouse gas, methane (CH<sub>4</sub>). Consequently pollution swapping can occur in which a promising solution to water pollution may exacerbate global warming through the release of CH<sub>4</sub>. Recent studies in rice paddies have shown that addition of alternative-electron acceptors in the form of sulphur- and iron-containing compounds will reduce CH<sub>4</sub> emissions. Hence this technique has the potential for limiting CH<sub>4</sub> emissions from constructed wetlands. Furthermore, it may be possible to utilise by-products from other situations to improve wetland performance and mitigate CH<sub>4</sub> emissions, resulting in a "win-win" situation. Iron can be added in the form of iron ochre, a by-product of mine water treatment and sulphur in the form of gypsum, a by-product of thermal power plant, or from recycled plasterboard.

The research examined, through controlled field and laboratory incubation studies, whether the addition of iron ochre (containing ferric oxide) and gypsum (calcium sulphate) reduces CH<sub>4</sub> emissions from a constructed wetland for treating farm runoff whilst maintaining nutrient removal. Using sediment incubation studies the effect of varying temperature on CH<sub>4</sub> suppression was also studied. Initial laboratory studies showed that ochre applied at a rate of 5t ha<sup>-1</sup> suppressed CH<sub>4</sub> emissions by 66 % at constant temperature and the CH<sub>4</sub> suppression increased with increasing temperature. In both constant and varying temperature laboratory experiments, gypsum had no effect on CH<sub>4</sub> suppression. The results from the preliminary study highlights the potential of the use of ochre in suppressing CH<sub>4</sub> emissions from constructed wetlands and also offers prospects for reusing by-products generated from other operations, which is a potential solution to both global warming and water pollution issues.

**Keywords:** Constructed wetlands, gypsum, iron ochre, methane, pollution swapping

### Introduction

Constructed wetlands are extensively used worldwide as a sustainable waste water treatment technology to intercept nutrients from agricultural runoff. Organic matter and nutrients are intercepted through various processes and are converted to various gaseous components. Methane (CH<sub>4</sub>) is one of the long lived greenhouse gas that is emitted from wetlands. The construction of wetlands to treat agricultural runoff may therefore inadvertently lead to a global warming issue due to enhanced release of these greenhouse gases, resulting in 'pollution swapping' (Reay, 2004).

The presence of alternative electron acceptors, such as O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup>, leads to competition for common electron donors, particularly H<sub>2</sub> and acetate, between bacteria using electron acceptors and methanogens (Lovely et al., 1987). The presence of either sulphate- or iron-reducers in an anoxic soil environment can out-compete methanogens and so limit CH<sub>4</sub> emissions (Van der gone and Neue, 1994). Several field and laboratory studies carried out in fresh water sediments, wetlands and rice paddies have reported that addition of sulphate and iron in different forms resulted in suppression of CH<sub>4</sub> emissions.

Air dried ferric oxide (ochre) - a by-product of acid mine drain treatment plant and calcium sulphate (gypsum) - a by-product of thermal power plant therefore have a potential use in limiting CH<sub>4</sub> emissions from wetlands. In this study the effects of iron ochre and gypsum application on CH<sub>4</sub> emissions from a constructed wetland were determined.

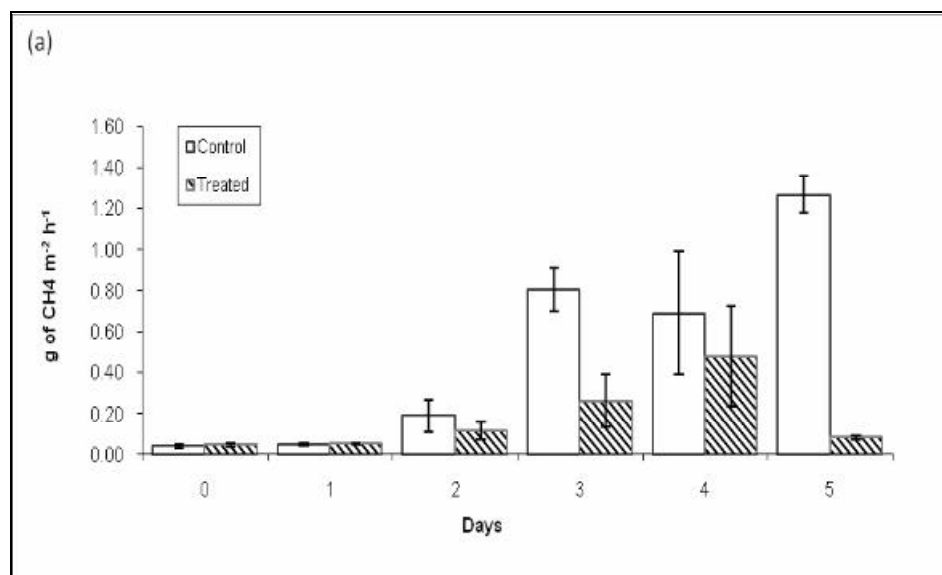
### Materials and Methods

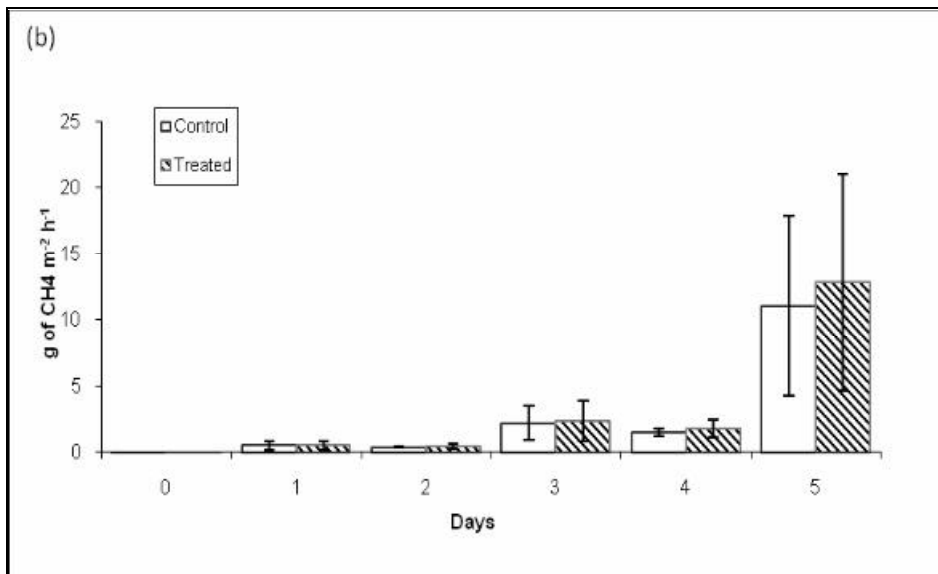
The results discussed in this paper form a part of a broader research which consists of both field and laboratory study. Only the laboratory study has been discussed in this paper. Sediment cores were collected in steel corers (diameter = 18 cm, height = 12 cm) from a constructed wetland located within

a Nitrate Vulnerable Zone in southeast Scotland (55°49' N, 2°13' W), which receives runoff from the farm yard, adjacent fields and septic tank effluent. The cores were collected monthly from March to June 2008. They were immediately sealed in a plastic bag to minimise moisture loss and were placed in a cool box (4°C) for transport to the laboratory. In the laboratory the sediment cores were transferred to Perspex cylinders (height = 40 cm, diameter = 19 cm) equipped with an air tight lid and gas sampling ports. Both cylinders were placed in a water bath and incubated for 4-5 days for acclimatisation before the experiment started. One of the cores was assigned as the control (no treatment) and the other received gypsum or ochre application at a rate equivalent to 5 t ha<sup>-1</sup>. In all experiments gas samples were collected at 3-hour intervals each day from the chamber head with a gas tight syringe. The headspace was flushed immediately after every sampling and the change in methane concentration between flushing and subsequent headspace sampling was used to calculate the accumulation rate of the CH<sub>4</sub>. The gas samples were analysed for CH<sub>4</sub> using a gas chromatograph with a flame ionisation detector (FID). Two experiments were conducted as follows. In the first study sediments were incubated after treatment for 10 days at constant in-situ temperature (gypsum treatment = 11.5 °C; ochre treatment = 7.5 °C) to identify the treatment effect. The second study aimed to identify the treatment effect under varying temperature. After acclimatisation at in-situ water temperature (gypsum treatment = 10 °C; ochre treatment = 7.5 °C) treatment was applied and then the temperature was increased by 5 °C at two days.

## Results and Discussion

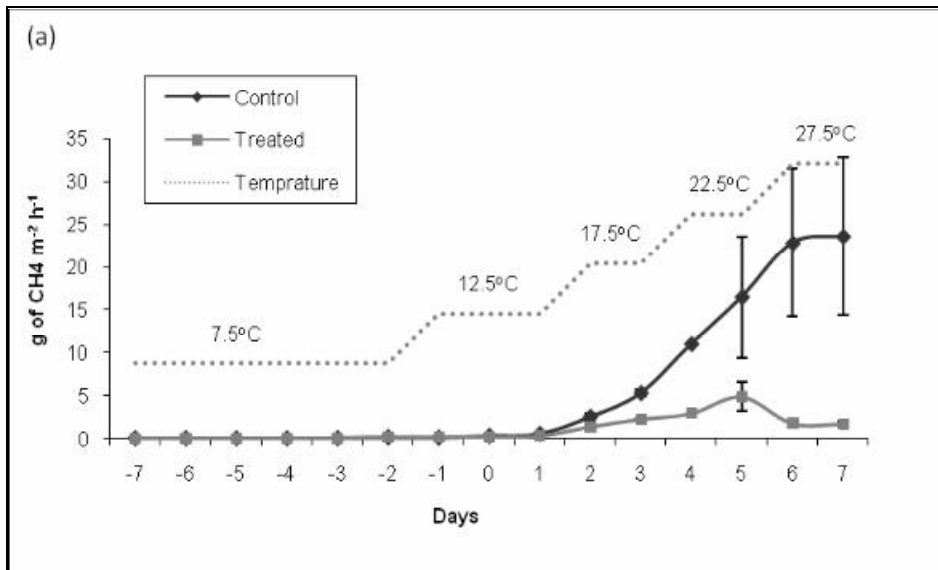
The effect of gypsum and ochre on CH<sub>4</sub> emissions are shown in Figure 1a and 1b respectively. CH<sub>4</sub> emission from the ochre treated core was low compared to those from the control core. On average cores treated with ochre emitted 0.173 g CH<sub>4</sub> m<sup>-2</sup> hr<sup>-1</sup> while control cores emitted 0.507 g CH<sub>4</sub> m<sup>-2</sup> hr<sup>-1</sup>, an apparent reduction of 66 %. Statistical analysis showed that the difference in CH<sub>4</sub> emissions between the treated and the control core was highly significant ( $P < 0.05$ ). This supports the hypothesis that iron additives stimulate iron reducers which suppress methanogens, results in a reduction in CH<sub>4</sub> emissions. In contrast CH<sub>4</sub> fluxes from the gypsum treated core were not significantly different from the control core over the entire incubation period ( $P = 0.884$ ). On average the cores treated with gypsum emitted 2.98 g CH<sub>4</sub> m<sup>-2</sup> hr<sup>-1</sup> which was similar to 2.6 g CH<sub>4</sub> m<sup>-2</sup> hr<sup>-1</sup> emitted from the control core (Figure 1b).

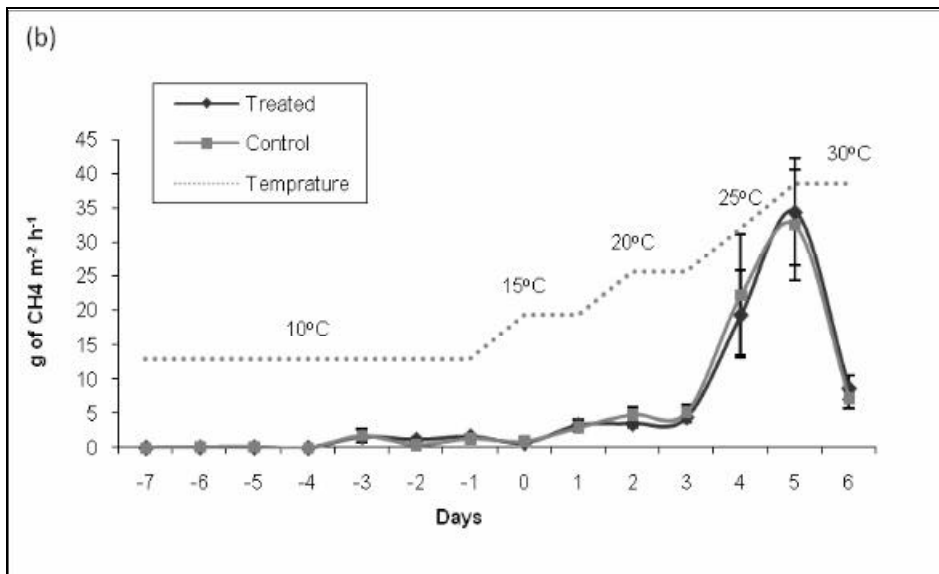




**Figure 1:** Methane emissions from sediment cores in days 0-5 of ochre (a) and gypsum (b) treatment experiments conducted at constant temperature (water bath temperature, ochre = 7.5 °C, gypsum = 11.5 °C). Day zero is the day when one of the cores received the treatment.

CH<sub>4</sub> emissions increased with increasing temperature in both the treatments (Figures 2a and 2b). This is likely to arise both from the direct effects of temperature on methanogenic activity and to increased anoxia in the sediments due to elevated heterotrophic respiration rates. With ochre treatment the CH<sub>4</sub> reduction efficiency increased with increasing temperature, rising from just over 50 % at 17.5 °C to over 90% at 27.5 °C respectively (Figure 2a). However there was no difference in the CH<sub>4</sub> emissions between the gypsum treated core and the control core over the entire incubation period under varying temperature (Figure 2b).





**Figure 2:** Methane emissions from sediment cores in the ochre and gypsum treatment experiments conducted at varying temperature. Day zero represents the addition of treatment (ochre in 2a and gypsum in 2b).

Reduced CH<sub>4</sub> evolution after gypsum and ferric iron application has been reported in several studies (Lindau et al., 1993; Lovley et al., 1987; Van der gone and Neue, 1994). The lack of CH<sub>4</sub> suppression observed in this study with respect to sulphate reducers could be because the sediment sulphate concentration did not reach the threshold necessary for successful competition between sulphate reducers and methanogens after addition of gypsum. Alternatively the wetland sediments had higher concentrations of sulphate and substrates, which facilitated simultaneous occurrence of methanogens and sulphate reducers.

## Conclusions

This study showed an average reduction of 66 % in CH<sub>4</sub> emissions from anoxic soil when treated with ochre at a rate of 5 t ha<sup>-1</sup>. It can be concluded that the suppression in CH<sub>4</sub> emissions by addition of ochre has significant potential as a means to reduce CH<sub>4</sub> emissions from constructed wetland soils and that further investigation into the longevity of this effect and its efficacy under field conditions is required.

## Acknowledgement

Authors would like to thank Andy Gray, John Morman, Ani Dwarakanath, Fabrice Gouriveau, Willena McAuley, Robert Howard and the farmer for help and support with the field and laboratory experiments.

## References

- Reay, D, S, 2004, "Fertilizer 'solution' could turn local problem global", *Nature* 427, 485
- Lindau, C, W, Bollich, P, K, DeLaune, R, Mosier, A, R, & Bronson, K, F, 1993, "Methane mitigation in flooded louisiana rice fields", *Biology and Fertility of Soils* 15, 174-178.
- Lovley, D, R, & Phillips, E, J, P, 1987, "Competitive mechanisms for inhibition of sulfate reduction and methane production in the zone of ferric iron reduction in sediments", *Applied and Environmental Microbiology* 53, 2636-2641
- Van der Gon, H, D, & Neue, H, U, 1994, "Impact of gypsum application on the methane emission from a wetland rice field", *Global Biogeochemical Cycles* 8,127-134