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Characterization of methane oxidation in a simulated landfill cover system by comparing molecular and stable isotope mass balances

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ABSTRACT

Biological methane oxidation may be regarded as a method of aftercare treatment for landfills to reduce climate relevant methane emissions. It is of social and economic interest to estimate the behavior of bacterial methane oxidation in aged landfill covers due to an adequate long-term treatment of the gas emissions.

Different approaches assessing methane oxidation in laboratory column studies have been investigated by other authors recently. However, this work represents the first study in which three independent approaches, ((i) mass balance, (ii) stable isotope analysis, and (iii) stoichiometric balance of product (CO_2) and reactant (CH_4) by CO_2/CH_4-ratio) have been compared for the estimation of the biodegradation by a robust statistical validation on a rectangular, wide soil column.

Additionally, an evaluation by thermal imaging as a potential technique for the localization of the active zone of bacterial methane oxidation has been addressed in connection with stable isotope analysis and CO_2/CH_4-ratios. Although landfills can be considered as open systems the results for stable isotope analysis based on a closed system correlated better with the mass balance than calculations based on an open system. CO_2/CH_4-ratios were also in good agreement with mass balance. In general, highest values for biodegradation were determined from mass balance, followed by CO_2/CH_4-ratio, and stable isotope analysis. The investigated topsoil proved to be very suitable as a potential cover layer by removing up to 99% of methane for CH_4 loads of 35–65 g m^{-2} d^{-1} that are typical in the aftercare phase of landfills. Finally, data from stable isotope analysis and the CO_2/CH_4-ratios were used to trace microbial activity within the reactor system. It was shown that methane consumption and temperature increase, as a cause of high microbial activity, correlated very well.

1. Introduction

Methane emissions from landfills are mainly affected by physical characteristics of the landfill cap and the entire site landfill gas collection (Christophersen et al., 2001). However, in case of several thousand old landfills in Germany and Europe, active gas extraction systems have never been applied (Ritzkowski et al., 2006). This would result in the uncontrolled emissions of methane to the atmosphere. Even if a gas extraction system is present, the gas recovery may be inconsistent. For example, in a study on Swedish landfills with gas extraction systems, the landfill gas recovery of the produced landfill gas was found to be highly variable with an average of 51% (Börjesson et al., 2009). Another study on field cells at three French landfill sites determined that the CH_4 gas recoveries were in the range of 41–94% of the theoretical CH_4 production and strongly depended on the presence and type of cover (Spokas et al., 2006). Thus, irrespective of the presence of an active gas extraction system, the mitigation of the remaining emissions is still important.

In general, possible solutions for the reduction of landfill gas emissions include the aeration of landfill waste (Ritzkowski et al., 2006), the utilization of biofilters, and the application of biocovers or soil covers as methane oxidation layer. Such systems are reviewed by Huber-Humer et al. (2008). Several field and laboratory studies have investigated the performance of methane

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oxidation by different systems and materials such as biofilters (Powelson et al., 2006; Powelson et al., 2007), biocovers (Abichou et al., 2006; Cabral et al., 2009; Capanema and Cabral, 2012; Mei et al., 2015; Scheutz et al., 2014), intermediate covers (Abichou et al., 2006), and soil covers (Barlaz et al., 2004; Bogner et al., 1997; De Visscher et al., 1999). These systems are helpful in reducing methane emissions especially in the aftercare phase of a landfill and beyond, when the utilization of the extracted landfill gas as energy source is no longer applicable due to its high CO_2/CH_4-ratio and consequently low energy density.

However, the required thickness of the methane oxidation layer is influenced by many factors which is reviewed by Huber-Humer et al. (2008) and Scheutz et al. (2009). Among these are the spatial and temporal variations of the soil's physical and chemical properties which have a strong impact on the soil gas transport and the methanotrophic activity (Scheutz et al., 2009). These include factors such as the soil temperature, moisture, and gas composition. At an old landfill in northern Germany, the influence of soil temperature, soil moisture, and barometric pressure on the soil gas composition was investigated (Gebert et al., 2011; Rachor et al., 2013). In order for a cover layer to effectively reduce methane emissions, it is important to understand and forecast its response to different environmental conditions. This requires characterizing the active zone of methane oxidation. Finding the active zone and identifying its dimensions within biofilters or cover layers, so as to predict alterations or shifts by changing conditions may be achieved by monitoring temperature and soil gas profiles (e.g., "intersection" of oxygen and methane concentrations, from CO_2/CH_4-ratios, and stable isotope analysis).

Another major challenge concerning these cover soils is to accurately determine how much methane they oxidize in order to control the cover soil's performance in terms of methane oxidation capacity and emission reduction in the field. As summarized by Chanton et al. (2009), different approaches exist for the estimation of methane oxidation. Methods for the estimation of the methane oxidation in landfill cover soils from stable isotope data have previously been described (Liptay et al., 1998). By means of mass balance and stable isotopes, the biodegradation of methane by biofilters has been investigated for different cover materials (Cabral et al., 2009; Capanema and Cabral, 2012; Powelson et al., 2006; Powelson et al., 2007). In a study by Christophersen et al. (2001), the emissions of CO_2 and CH_4 from an old landfill and their lateral gas transport into adjacent soil were investigated by balancing the gas flux with the CO_2/CH_4-ratios. Based on a similar methodology, Gebert (2011) investigated the methane oxidation of laboratory columns filled either with mineral soil or two different types of compost. Another available technique is the gas push-pull test. It was introduced by Urmann et al. (2005) and has been improved for the application in the field (Streese-Kleeberg et al., 2011) at different landfills and during different seasons. While several investigations have been applied already, they most often compare only two techniques at a time, namely mass balance and an alternative method. A thorough approach comparing the calculated fraction of oxidized methane by stable isotope analysis, mass balance, and CO_2/CH_4-ratio has not been performed, so far.

The aim of this study was to investigate the oxidation potential of a reactor plate system during the simulation of three typical scenarios encountered in the aftercare phase of a landfill.

The three scenarios included (i) a standard situation for a methane oxidation layer of a landfill in its aftercare period with relative low gas loads of methane and carbon dioxide ("normal" state). (ii) A local increase in gas load as can be observed on landfills, e.g. due to vegetation (soil penetration by roots) or settling of the deposited waste material (degradation of high organic waste), leading to preferential flow ("hotspot"). (iii) Decrease in temperature due to seasonal factors ("cooling").

Additionally, biodegradation calculated by different techniques including stable isotope analysis, mass balance, and CO_2/CH_4-ratios are compared.

2. Materials and methods

2.1. Reactor plate

The reactor system was constructed of a stainless steel framework which was capped with a Plexiglas facing on the front and the rear side. Its dimensions were 12 cm, 200 cm, 150 cm (length, width, height). Inside, a 15-cm layer of small circular plastic bodies was placed at the bottom of the reactor plate which served as a gas distribution layer. It was covered with $\sim$0.26 m^3 topsoil (water content: 9.7% w/w, organic dry substance: 2.2% w/w determined from 30 g soil by standard method DIN 12880, 2001). This methane oxidation layer had a height of 110 cm leaving a total headspace of $\sim$25 cm. The reactor was supplied with humidified gases to avoid desiccation of the soil body. Methane and carbon dioxide of 3.5 (99.95%) purity (both Airliquide, Düsseldorf, Germany) were added at the bottom of the reactor by ten evenly distributed Rauclair-E PVC inlet tubings (Rehau AG&Co, Rehau, Germany). These inlets were amended with three-way stopcocks (Sarstedt AG und Co., Nümbrecht, Germany) to either allow gas flow or to close the feeding. At the top, air was added by seven inlets. The volume flows of the entering gases were regulated by mass flow controllers (Bürkert, Ingelfingen, Germany). Excess gas exiting the reactor by six exhaust lines was quantified by a mass flow monitor (Bürkert, Ingelfingen, Germany). The experimental setup is depicted in Fig. 1.

Three different scenarios were investigated with the reactor plate. These included the normal state with regular gas flow ("normal"), an increase in local CH_4 gas load ("hotspot"), and the cooling of the atmospheric gas phase ("cooling"). The "normal" state should simulate a standard situation for a methane oxidation layer of a landfill in its aftercare period with relative low gas loads of methane and carbon dioxide. In case of the "hotspot", the outer three gas inlets at the bottom of both sides of the plate were shut while leaving the remaining four in the middle open. Thus, the entering gas flow was focused in the center of the plate. The "cooling" should simulate a decrease in temperature due to seasonal factors. A recovery period was included when changing from "hotspot" to "normal". Between "normal" and "cooling" the reactor was shut down for the installation of two heat exchangers cooling the incoming airstream. A glycerin water mixture served as cooling agent circulating in the system. Gas loading conditions are indicated in Table 1.

2.2. Sampling from the reactor plate

For the investigation of the biodegradation of methane, both the inlet gas (at 148.5 cm from the top of the reactor) and the headspace (at 6.5 cm from the top of the reactor) were sampled. For a more detailed description of the reactor setup, see supplemental material.

2.3. Thermal imaging

Thermal imaging was performed using a testo 875-1i thermographic camera (Testo SE & Co. KGaA, Lenzkirch, Germany). In order to reduce the possibility of thermographic artefacts formed by light scattering and reflection, the front was finished with a black varnish (see Fig. 1 right). Calibrating the thermographic camera was performed for "heated surfaces" in an air-conditioned room in which the laboratory experiment was conducted. The surrounding room temperature and the surface temperature of the

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