Environmental Pollution 157 (2009) 3508–3513

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Nitrous oxide supersaturation at the liquid/air interface of animal waste

Konstantinos C. Makris [a,*], Syam S. Andra [b], Michael Hardy [c], Dibyendu Sarkar [c], Rupali Datta [d], Stephan B.H. Bach [e], Conor P. Mullens [e]

[a] Cyprus International Institute for the Environment and Public Health in association with the Harvard School of Public Health, 5 Iroon Street, Nicosia 1105, Cyprus
[b] Environmental Geochemistry Laboratory, University of Texas at San Antonio, San Antonio, TX, USA
[c] Department of Earth and Environmental Studies, Montclair State University, Montclair, NJ, USA
[d] Department of Biological Sciences, Michigan Technological University, Houghton, MI, USA
[e] Department of Chemistry, University of Texas at San Antonio, San Antonio, TX, USA

*Temperature-dependent $N_2O$ supersaturation at the liquid/air interface of animal waste.*

ARTICLE INFO

*Article history:*
Received 17 March 2009
Received in revised form
18 May 2009
Accepted 3 June 2009

*Keywords:*
Animal waste
Henry constant
Lagoons
Liquid/air interface
Nitrous oxide
Supersaturation

ABSTRACT

Concentrated animal feeding operations around the globe generate large amounts of nitrous oxide ($N_2O$) in the surrounding atmosphere. Liquid animal waste systems have received little attention with respect to $N_2O$ emissions. We hypothesized that the solution chemistry of animal waste aqueous suspensions would promote conditions that lead to $N_2O$ supersaturation at the liquid/air interface. The concentration of dissolved $N_2O$ in poultry litter (PL) aqueous suspensions at 25 °C was 0.36 μg $N_2O$ $mL^{-1}$, at least an order of magnitude greater than that measured in water in equilibrium with ambient air, suggesting $N_2O$ supersaturation. There was a nonlinear increase in the $N_2O$ Henry constants of PL from 2810 atm/mole fraction at 35 °C to 17 300 atm/mole fraction at 41 °C. The extremely high $N_2O$ Henry constants were partially ascribed to $N_2O$ complexation with aromatic moieties. Complexed $N_2O$ structures were unstable at temperatures > 35 °C, supplying the headspace with additional free $N_2O$ concentrations.



## 1. Introduction

Anthropogenic emissions of nitrous oxide ($N_2O$) to the atmosphere constitute a major fraction of the global $N_2O$ emissions, contributing to the observed global warming (IPCC, 1997). While $CO_2$ is the main greenhouse gas receiving most of the regulatory agencies' attention, $N_2O$, a by-product of nitrogen fertilization in agriculture is also attracting attention due to its 300 times larger global warming potential than an equal mass of $CO_2$. According to the Intergovernmental panel on climate change (IPCC), anthropogenic sources of $N_2O$ are classified into: i) direct $N_2O$ emissions from soils amended with nitrogenous compounds, ii) direct emissions from animal waste management systems and iii) indirect $N_2O$ emissions (runoff and/or leaching to surface- and groundwater, volatilization, etc.). Global anthropogenic $N_2O$ emissions from agriculture totaled ~6 Tg $N_2O$–N in 1994 (~75% total anthropogenic emissions), with equal contributions among the three mentioned agricultural systems (direct emissions, animal waste management, and indirect emissions) (IPCC, 1997; Kroeze et al., 1999).

Global budgets for greenhouse gases are of utmost importance in advancing our understanding of their effects on global warming. Estimated concentration ranges for known anthropogenic $N_2O$ sources cannot explain the observed $N_2O$ atmospheric increase (Watson et al., 1992). There is a large difference between the low $N_2O$ yield (1% of fixed N input) in agricultural fields and the much larger value (4% of fixed N input) calculated from the global $N_2O$ budget (Kroeze et al., 1999). Discrepancies between in-situ $N_2O$ yields from agricultural fields and those obtained from life cycle/budget analyses, suggest considerable $N_2O$ production beyond agricultural fields, such as, rivers, estuaries, and concentrated animal feeding operations (CAFOs) (Kroeze et al., 1999; Schlesinger et al., 2006). The presence of appreciable changes in total N storage on land shows that the N budget is not in steady state, affecting the magnitude of drainage and denitrification exports of N (Van Breemen et al., 2002). Increased fertilizer-N input in agricultural soils puts a burden on receiving streams and rivers, acting as important sinks for bioavailable $N_2O$, or as carriers for transport of dissolved $N_2O$ towards the downstream coastal water bodies (Mulholland et al., 2008).

Concentrated animal feeding operations around the globe generate large amounts of $N_2O$ in the surrounding atmosphere of composted or land-applied animal waste (Czepiel et al., 1996). Liquid animal waste systems or storage lagoons have received little

* Corresponding author. Tel.: +357 224 49292; fax: +357 224 49293.
*E-mail address:* kcmakris@gmail.com (K.C. Makris).

0269-7491/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envpol.2009.06.006

attention for their contribution to $N_2O$ emissions. Most of the $N_2O$ research in animal waste management systems has been focused on headspace $N_2O$ dynamics in low-moisture animal waste (Coyne et al., 1994; Akiyama and Tsuruta, 2003), overlooking the partitioning of $N_2O$ in the liquid phase and the effect of solution chemistry on $N_2O$ emissions. Preliminary experiments in our laboratory documented the $N_2O$ supersaturation in wastewater suspensions collected from swine wastewater lagoons nearby CAFOs (Makris et al., 2009). This preliminary dataset urged us to systematically investigate the environmental conditions that support $N_2O$ supersaturation in animal wastewater suspensions.

The objectives of this study were to: i) determine the degree of $N_2O$ supersaturation and partitioning at the liquid/air interface of animal waste; and ii) evaluate the conditions that promote increased $N_2O$ concentrations at the liquid/air interface of animal waste.

## 2. Materials and methods

### 2.1. General properties of the waste

The poultry litter (PL) was kindly supplied by Dr. J.H. Grove (Univ. of Kentucky). The fresh PL was collected from a poultry farm in Kentucky, USA, and was stored at 4 °C to minimize microbial activity. The PL was passed through a 2-mm sieve before use in the $N_2O$ experiments. Determination of percentage solids was performed by drying the PL at 105 °C for 48 h (Rhoades, 1996). Total elemental analysis of the PL was performed by ICP-MS on acid-digested samples according to the USEPA method 3050B (USEPA, 2000).

### 2.2. Nitrous oxide evolution kinetics in PL

The PL aqueous suspension samples were prepared via a routine water extraction scheme to facilitate partitioning of the evolved $N_2O$ between the liquid and the gaseous phase (pre-heating step). The PL samples (0.3 g equivalent dry weight) were shaken (120 rpm) with 6 mL of deionized water (d-$H_2O$) for 24 h at 25 °C in gas-tight GC sample vials (25 mL). The 25 mL sample vials were equipped with Mininert™ precision 20-mm sampling caps (Restek Corporation, Bellefonte, PA, USA). The vial caps were frequently changed with new septa (Restek Corporation, Bellefonte, PA, USA). After the 24 h equilibration at 25 °C, a Hamilton microliter gas-tight syringe was used to withdraw 1 mL of headspace for $N_2O$ analysis (pre-heating step), headspace was brought to atmospheric pressure by opening the vial, and the sample vials containing the suspension were subsequently centrifuged to separate the liquid from the solid phase (4000 g for 20 min).

Immediately after the pre-heating step (used to produce a detectable amount of $N_2O$ from PL), a post-heating step was initiated to strip the $N_2O$ from solution into the headspace. The post-heating step consisted of transferring 3 mL of the already centrifuged supernatant liquid phase into a 25-mL glass vial containing 3-mL of d-$H_2O$, ensuring a constant headspace volume (19 mL), similar to the pre-heating step. These vials were subjected to a thermal equilibration technique to determine dissolved $N_2O$ concentrations in the PL aqueous suspensions. The thermal equilibration scheme was optimized by varying the shaking time (0.5, 1, 2, 4, 8 16, 32, 48 h) and temperature (25, 41 and 70 °C) of the PL incubated samples in a temperature-, and speed-controlled incubator (Boekel Scientific, Feasterville, PA, USA). At select sampling intervals, 1 mL of headspace was withdrawn with a gas-tight syringe and manually injected into a GC–MS (Trace 2000 GC with a PolarisQ mass spectrometer, ThermoFinnigan, San Jose, CA, USA). The separation of $N_2O$ and $CO_2$ was achieved using an Rt-QPLOT capillary column (DVB PLOT, 30 m × 0.32 mm i.d., Restek Corporation, Bellefonte, PA, USA). Preparation of nitrous oxide standards and sample injections were performed with a wide range of gas-tight syringes (2.5–5000 μL) (Hamilton, Co., Reno, NV, USA). A microMAT-14 1 ppm (v/v) $N_2O$ gas standard in $N_2$ was used as the $N_2O$ source for the experiments (Matheson Tri-Gas Inc., Twinsburg, OH, USA); the gas cylinder was equipped with a pressure regulator and syringe adaptor.

### 2.3. Nitrous oxide analytical protocol

The $N_2O$ analytical protocol was modified after the Accorsi et al. (2001) method. Nitrous oxide gas separation and quantification using GC–MS was achieved with a linear gradient: 0–3 min at 40 °C, ramp to 50 °C at 20 °C $min^{-1}$, 0.5 min at 50 °C, ramp to 100 °C at 100 °C $min^{-1}$ and held at 100 °C from 4.5 to 9.5 min. The sample injection volume was 1 mL of headspace. During analysis, the detector was off from 0 to 2 min to avoid the $CO_2$ gas (1.91 min) from overloading the detector and potentially masking the $N_2O$ chromatographic peak, which appeared at 2.21 min. The headspace gas sample was introduced in the column with a split injection port (1: 10 split ratio) at 150 °C. High purity He gas (Praxair, Praxair, Inc., Danbury, CT, USA) was used as the collision gas at a constant flow rate (1 mL $min^{-1}$). Electron impact ionization was employed for the mass spectrometric identification of volatile compounds; the ionizer was held at 200 °C. The mass spectrometer was operated in full scan mode between $m/z$ 35 and 650. Total ion chromatograms (TIC) of each run were used to derive the peak area of $N_2O$ for quantification.

### 2.4. Multiple headspace extractions

The animal waste samples were subjected to a stepwise gas extraction procedure called multiple headspace extraction (MHE) for determining partition coefficients and Henry constants of $N_2O$ in PL aqueous suspensions (Kolb, 1982; Chai and Zhu, 1998). Glass vials (25 mL vial volume) containing the PL aqueous suspensions (0.3 g PL with 6 mL d-$H_2O$) were capped with Mininert™ precision 20-mm sampling caps and incubated at 25 °C for 24-h. Sample vials were centrifuged (4000 × g for 20 min), and 3 mL of the clear supernatant were then transferred to another GC sample vial containing 3 mL of d-$H_2O$. Subsequently, the vials were thermostated at either 25, 35, 38, 41, 55, or 70 °C for 2-h in a temperature and speed-controlled incubator (Boekel Scientific, Feasterville, PA, USA). The 2-h thermal equilibration time was selected from preliminary kinetic experiment that showed no additional $N_2O$ production by extending the shaking time up to 72-h, suggesting that microbial-mediated $N_2O$ generation was not observed in the post-heating step (data not shown). After the 2-h equilibration at the selected temperature, $N_2$ gas was used to pressurize the vial and a pressure-locked gas syringe was used to withdraw a specific amount of headspace gas (1 mL). The vial was opened for a few seconds to allow the vial pressure to be released into the atmosphere. Because of the equilibrium disturbance, the vial was subjected to a subsequent second thermal equilibration step (under the same conditions), and so forth until a satisfactory number of extraction steps was acquired (Kolb and Ettre, 2006). Measurement of pressure changes was not required to calculate analyte concentration in the headspace following the procedure and equations given in Kolb and Ettre (2006). The change in analyte volume in the headspace due to heating and extraction was considered minimal following the explanation given by Chai and Zhu (1998) that used the same method.

The liquid/air $N_2O$ partition coefficient of PL aqueous suspensions ($K$) was calculated from the MHE data using the following formula (Kolb and Ettre, 2006):

$$K = ((Q_{std} - Q_s)/(Q_{std} - 1))^*\beta. \quad (1)$$

The $Q_{std}$ and $Q_s$ equal to $e^{-q}$, where $q$ is the slope of the linear regression plot of the ln(area counts) as a function of the extraction steps for the standard and sample vials, respectively; the $\beta$ is the liquid/air phase ratio. The standard vial corresponds to an empty sample vial that contained 25 μL $N_2O$ and was treated similarly to the sample vials. The respective Henry constants were taken as the reciprocal of the partition coefficient $K$.

### 2.5. Quantification of dissolved $N_2O$ in PL suspensions

The PL aqueous suspensions were subjected to the above mentioned thermal equilibration technique to determine dissolved $N_2O$ concentrations using the MHE method. The concentrations of the dissolved $N_2O$ in the PL aqueous suspensions were calculated from the experimentally measured partition coefficients using the procedure by Kolb and Ettre (2006). In brief, both MHE data for the sample and the standard vial were used. The intercept ($Ai^*$) from the semi-logarithmic plots (MHE data) was converted to absolute area counts. The sum of the area counts for each extraction step was calculated from:

$$\text{sumAi} = Ai^*/(1 - Q). \quad (2)$$

A volume correction factor was included between the standard (no liquid) and sample vials (6 mL liquid). The sumAi for the standard vial was multiplied by the volume correction factor to get the corrected sumAi for the standard vial. The micrograms of $N_2O$ in the sample vial were calculated by dividing the sumAi for the sample by the corrected sumAi for the standard vial, and multiplying by the μg of $N_2O$ initially added in the standard vial. The dissolved $N_2O$ concentrations in the PL aqueous suspensions were then calculated from the partition coefficient equation (Table 1).

## 3. Results and discussion

### 3.1. Multiple headspace extractions of $N_2O$

Detailed chemical characterization of the poultry litter sample is given in Makris et al. (2008). In brief, total C and N content was 320 and 84 g $kg^{-1}$ respectively. Significant amounts of total Al (2900 mg $kg^{-1}$) and Fe (500 mg $kg^{-1}$) were present, and the operationally defined oxalate extractable Al and Fe concentrations were 1050 and 360 mg $kg^{-1}$, respectively. The nitrous oxide