Science of the Total Environment 601–602 (2017) 83–88

Contents lists available at ScienceDirect

Science of the Total Environment

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

Quantification of nitrous oxide in wastewater based on salt-induced stripping

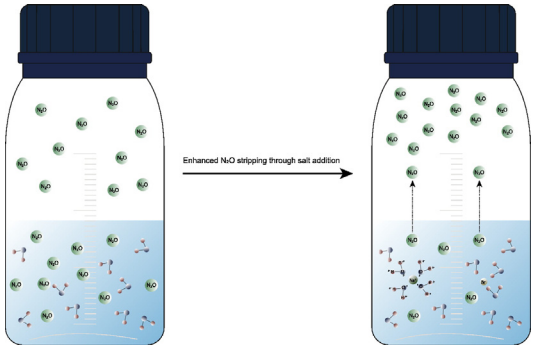
Pascal Kosse [a,*], Manfred Lübken [a], Torsten C. Schmidt [b,c], Marc Wichern [a]

[a] Institute of Urban Water Management and Environmental Engineering, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany
[b] Instrumental Analytical Chemistry, University of Duisburg-Essen, Universitätsstraße 5, 45141 Essen, Germany
[c] Centre for Water and Environmental Research (ZWU), University of Duisburg-Essen, Universitätsstraße 2, 45141 Essen, Germany

HIGHLIGHTS

- A salt-induced stripping method for the quantification of liquid N_2O is proposed.
- The addition of the inorganic salt NaBr approved most suitable for N_2O stripping.
- By applying the proposed method, N_2O could be proven during BNR at WWTP level.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 January 2017
Received in revised form 3 May 2017
Accepted 5 May 2017
Available online xxxx

Keywords:
Salt-induced stripping
Nitrous oxide
Sodium bromide
Ultrasound
Greenhouse gases

ABSTRACT

Monitoring nitrous oxide (N_2O) emissions from wastewater treatment plants has attracted much attention in recent years demanding accurate and rapid quantification methods. In the present study a salt-assisted methodology is proposed by which N_2O is chemically stripped out from wastewater and quantified by gas chromatography (GC-TCD) subsequently. Eight different inorganic salts have been evaluated for this purpose, likewise the application of ultrasound. By addition of sodium bromide (NaBr) the best recovery rate of about 98% ($=1.14 \pm 0.05$ kg·m^{-3}) N_2O from a saturated stock solution (1.16 kg·m^{-3}, 295.85 K and 1 atm) was achieved. The application of ultrasound led to considerable smaller N_2O recoveries of 37% ($=0.43 \pm 0.01$ kg·m^{-3}) after a 60 min treatment. Practical applicability of the method has been demonstrated by applying NaBr to grab samples from a municipal wastewater treatment plant. The highest N_2O concentration was found in the secondary clarifier with 10.99 ± 0.20 g·m^{-3}. Besides, N_2O could be quantified in the activated sludge process with up to 9.87 ± 0.50 g·m^{-3} yielding 7.75 g $N_2O \cdot PE^{-1} \cdot a^{-1}$ specifically for the investigated wastewater treatment plant. Hence, the proposed method proved suitable as a routine quantification method for N_2O.

1. Introduction

Global climate change is a process that can be attributed to the release of anthropogenic greenhouse gases into the atmosphere, and affects severely our modern society in various ways. The main gaseous contribution comes from carbon dioxide (CO_2), methane (CH_4) and

* Corresponding author.
E-mail address: pascal.kosse@rub.de (P. Kosse).

http://dx.doi.org/10.1016/j.scitotenv.2017.05.053
0048-9697/

nitrous oxide (N_2O). Among these three gases, nitrous oxide is the most powerful one with regard to its high global warming potential (GWP_{100}) of 264 contributing about 6–10% to the global warming effect (Musenze et al., 2014; Short et al., 2014). Wastewater treatment plants (WWTPs) are known to be one of many potential contributors for nitrous oxide. At present, 2.8% of the anthropogenic N_2O is emitted from wastewater treatment plants, while between 2005 and 2020 the global N_2O emission from wastewater treatment is expected to increase by 13% (Law et al., 2012).

In the framework of today's wastewater treatment, N_2O is an obligate intermediate during biological nitrogen removal (BNR). During autotrophic nitrification N_2O can be produced either by ammonia-oxidizing bacteria (AOB) through the oxidation of the intermediate product hydroxylamine (NH_2OH), or through the conversion of nitrite (NO_2^-) during the aerobic nitrous denitritation pathway (Weißbach et al., 2017). Regarding heterotrophic denitrification, N_2O is produced as the last intermediate before molecular nitrogen (N_2) is emitted from the BNR. Recently it could be shown that N_2O can even occur during anaerobic ammonium oxidation (Anammox), since N_2O is the precursor of the metabolic intermediate hydrazine (N_2H_4) (Kampschreur et al., 2008; Schneider et al., 2011).

Reported N_2O emissions from wastewater treatment plants vary strongly between 0% and 25% of the influent nitrogen load depending on the design and operation of the plants, the flow and the characteristics of wastewater (Benckiser et al., 1996; Foley et al., 2009; Kampschreur et al., 2008; Kosonen et al., 2016; Law et al., 2012; Mikola et al., 2014). Several particular circumstances lead to these emissions, such as N_2O stripping due to active aeration, transition between anoxic and aerobic conditions, imposition of anoxia on nitrifying bacteria, lack of organic carbon and copper (Law et al., 2012; Wu et al., 2014).

Given its high impact on the climate and the increasing release of emissions from the wastewater sector at varying concentration levels there's an increasing demand for standardized and accurate quantification methods (Law et al., 2012; Schneider, 2013). Reported quantification methods for the liquid phase mostly comprise floating hoods, headspace approaches, or Clark-type N_2O microsensor, while gaseous N_2O is mostly measured using open-path Fourier-transform infrared spectroscopy (FTIR) (Kosse et al., 2016; Marques et al., 2014; Marques et al., 2016; Short et al., 2014). The latter technique has proven its reliability and applicability many times (Kosonen et al., 2016; Mikola et al., 2014), but measuring the dissolved N_2O concentration is likely to yield more information as the N_2O formation occurs in the liquid phase (Mampaey et al., 2015). Besides these technical approaches also emissions factors can be used (Giltrap et al., 2013), but those are more prone to uncertainties.

The solubility of N_2O in the liquid phase is determined by three factors: temperature, environmental pressure above the liquid phase and the salinity. Taking advantage on the latter one forms the basis for a salt-assisted stripping methodology for N_2O. The solubility of N_2O in water is caused by the formation of a hydration shell surrounding the gas molecules. This effect is driven by dipole-dipole interactions between the water molecules and the nitrous oxide molecules. However, dipole-dipole interactions (5–50 $kJ \cdot mol^{-1}$) are weak forces compared to ion-dipole ones (50–200 $kJ \cdot mol^{-1}$), since the charge of any ion is much greater than the charge of solely polar molecules (Tiwari and Uzun, 2015). When adding ionic compounds to a nitrous oxide containing sample, the ion-dipole forces will lead to a salting out of N_2O. Once it has transferred from the liquid phase into the gas phase it can easily be quantified using gas chromatography.

The proposed methodology would offer a variety of benefits for the practice. In first place nitrous oxide will be quantified where it is actually produced – in the liquid phase. Depending on the desired monitoring strategy grab samples could be taken from the wastewater treatment plant in dependency of the hydraulic retention time or at the same time at different treatment units. Besides, grab sampling has been stated to yield a relatively precise measure of the true wastewater N_2O concentration (Daelman et al., 2013; Short et al., 2014). Particularly sampling in dependency of the hydraulic retention time (HRT) is problematic when using either N_2O microsensors or FTIR devices. There are also some more direct advantages regarding other established methods such as headspace analysis. The headspace approach is a well-established analytical method that is frequently used for the quantification of volatile organic compounds (VOC) demanding a phase equilibrium of the analyte between the liquid and the gas phase. Knowledge of the air-water partition coefficient (K_{aw}) is important in order to calculate the concentration in the liquid phase. Currently there is no K_{aw} value available in literature, particularly for the wastewater matrix that underlies a diurnal variation. The salt-induced stripping approach overcomes this, as the inorganic salt shall lead to a completely stripping of N_2O into the headspace circumventing the missing K_{aw} value and the diurnal character of wastewater.

Finally, as N_2O can be seen as an early warning indicator for a poorly functioning biological treatment, the proposed method can be used as a rapid test on a regular basis without installing expensive online technology. This might be of particular interest for operators of WWTPs where the focus is less on continuous N_2O monitoring.

A salt-assisted quantification approach has already been performed once for dissolved methane in wastewater by Daelman et al. (2012), who performed a modification of the approach as described by Gal'chenko et al. (2004). Since Daelman et al. (2012) focused on investigating methane emission dynamics at a full-scale WWTP using mass balances, method development was unfortunately not performed. Inspired by the approach from Daelman et al. (2012), the present study aims to develop an easily-deployable, low-cost direct quantification method for dissolved nitrous oxide in wastewater samples by exploiting the salting-out effect. Method development is performed following DIN 38402 and DIN 32645. An ultrasound application is additionally performed as a physical counterpart to the chemical approach. The methods practical applicability is validated by analyzing wastewater samples from a municipal wastewater treatment plant.

2. Materials and methods

2.1. Properties and selection criteria of inorganic salts

The inorganic salts evaluated within the present study were chosen according to specific properties: (1) the inorganic salt needs to have a continuously high solubility within a temperature range of 273.15 K–313.15 K and at a pH value that is close to the one of wastewater (approx. pH ≈ 7), (2) the salt is not classified as environmentally hazardous, (3) no chemical side reactions are expected or known that lead to the production or consumption of N_2O, (4) inorganic salts yielding high-valence ions are preferred over ions having a valence of one, since they tend to have a stronger salting-out effect (Stoessell and Byrne, 1982). Besides, the ion valence is also linked to the ion strength, which should be high as well, (5) when the inorganic salt becomes dissolved it should not react substantially endothermic or exothermic so that the temperature does not affect the stripped gas volume.

Since it is intended to add the inorganic salts at their maximum chemical solubility, no potential biological feedback as described, for instance, by Tsuneda et al. (2005) is expected that could influence the results. On the contrary, it is expected that every microbial activity affecting N_2O production or consumption is inhibited.

The tested inorganic salts within this present study based upon the before mentioned prerequisites were sodium bromide (NaBr, >99%, Fischer Scientific, Loughborough, UK), sodium chloride (NaCl, ≥99.5%, Carl Roth GmbH + Co. KG, Karlsruhe, Germany), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$, 99.9%, AnalaR NORMAPUR, VWR International, Radnor, PA, USA), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, ≥99%, Carl Roth GmbH + Co. KG, Karlsruhe, Germany), magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, ≥99%, AnalaR NORMAPUR, VWR International, Radnor, PA, USA), iron(III) chloride