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Research Article

Bioscrubber treatment of exhaust air from intensive pig production: Case study in northern Germany at mild climate condition

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Treatment by field-scale bioscrubber of exhaust air, including ammonia (NH₃) and the greenhouse gases methane (CH₄), nitrous oxide (N₂O), and carbon dioxide (CO₂), from 13 intensive pig production houses located in northern Germany were investigated in 2013 and 2015. NH₃ removal efficiencies varied between 35 and 100% with an overall average value of 79% under the NH₃ inlet fluctuations from 34 to 755 g d⁻¹ m⁻³ in both 2013 and 2015. Results of the electron microscopic analyses demonstrated that the bacteria *Nitrosomonas* sp. and methanotrophs *type I* were the dominant NH₃ and CH₄ oxidizers, respectively. However, overall average removal efficiencies of CH₄ was approximately zero, which means CH₄ is hard to remove in bioscrubbers under normal operation. The pH of recirculation water in the bioscrubber varied from 6.1 to 8.1, and the bioscrubbers with low pH values (<7.0) had high NH₃ removal efficiencies (>79%). Electrical conductivity was commonly used to diagnose the bioscrubbers' performance; in the present study, electrical conductivity presented a significant linear relationship with dissolved inorganic nitrogen, which indicates the performance stability of the 13 selected bioscrubbers.

Keywords: Ammonia / Bioscrubber / Methane / Microorganism / Pig house

Received: July 1, 2016; *revised:* August 25, 2016; *accepted:* October 12, 2016

DOI: 10.1002/elsc.201600169

1 Introduction

The environmental impact of exhaust gas emission of ammonia (NH₃) and the greenhouse gases methane (CH₄), nitrous oxide (N₂O), and carbon dioxide (CO₂) from intensive livestock production has been attracting people's concern over the past decade [1]. NH₃ emissions are related to the risk of soil acidification and of water pollution owing to the high nitrate (NO₃⁻) concentration resulting from nitrification, which is the microbial oxidation of NH₃. Compared to CO₂, whose global warming potential is 1, CH₄ and N₂O substantially contribute to the greenhouse effect with their Global Warming Potentials (GWPs) of 23 and 296, respectively [2]. Thus, finding an economic and stable technique and ensuring effective treatment are crucial to reduce the negative effect of exhaust gas emitted from intensive animal farm.

It was reviewed by Hamon et al. [3] that wet scrubbers, bioscrubbers, and biofilters have become the widely used technologies

for intensive pig house exhaust gas treatment. Germany is one of the largest pig production (27.69 million per year) countries in Europe [4]. As of 2010, biofilters, trickle bed filters (bioscrubbers), and multistage operations amounted to 26.4, 24.0, and 43.2% of the total accumulation exhaust air treatment systems installed in Germany, most of which were installed on pig farms. In particular, trickle bed filters (bioscrubbers) showed a clear increasing tendency for utilization because of the robust, sustainable, and low-cost characteristics of the technique [5]. Therefore, reliable assessments on field-scale bioscrubbers in different years were necessary to approve the application of this approach.

Previous research on bioscrubber applications mainly focused on NH₃ treatment that converts NH₃ into nitrite (NO₂⁻) and NO₃⁻ through nitrification in the water, and further transforms into N₂ through denitrification (Fig. 1A) [6, 7]. Field-scale bioscrubbers can normally achieve 42–99% NH₃ removal efficiencies [8–10]. For climate-relevant trace gases, such as CH₄, N₂O, and CO₂ treatment, previous study reported that CH₄ and CO₂

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Abbreviations: EC, electrical conductivity; BS, bioscrubber; ICM, intracytoplasmic membrane

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Figure 1. (A) Biochemical pathways of NH_3 oxidation, $\rightleftharpoons$ means nitrification, $\rightarrow$ means denitrification; (B) biochemical pathways of CH_4 oxidation.

cannot be removed, and that N_2O has a one to seven times higher effluent concentration in a biotrickling filter (bioscrubber) when treating the exhaust air from a pig house in Canada [8]. However, the theoretical biochemical reaction pathways of CH_4 (Fig. 1B) illustrate that CH_4 can be initially oxidized to methanol (CH_3OH) and then oxidized to intermediate compounds of formaldehyde (HCHO), formate (HCOOH), and finally to CO_2 by methanotrophic bacteria [11]. Thus, the removal of climate-relevant trace gases and the relative functional bacteria in bioscrubber systems were also needed to be investigated.

Niedersachsen in northern Germany, especially the area of Cloppenburg, is one of the main pig production areas in Europe, contributing around 19% of the pig production in the continent [1]. Therefore, in the present study, 13 field-scale bioscrubber plants from this area were selected to assess the removal ability and stability of NH_3 and of climate-relevant trace gases CH_4 , N_2O , and CO_2 in 2013 and 2015. The simultaneous parameters of recirculated water in the bioscrubbers were also investigated. Furthermore, the dominant NH_3 - and CH_4 -oxidizing

bacteria were first detected in selected bioscrubbers by electron microscopy, to help us to deeper understand the mechanisms of NH_3 removal.

2 Materials and methods

2.1 Description of pig houses and bioscrubbers

The research was conducted in 13 intensive pig production houses located in northern Germany (Lower Saxony, Cloppenburg, Niedersachsen) in 2013 and 2015. Each pig house was equipped with the same mechanical ventilation channel (Fig. 2A) and a bioscrubber (Fig. 2B). As shown in Fig. 2A, fresh air entered the pig house through windows and mixed with the inside air. After passing through a slatted floor over the slurry pits, the mixed air exited through an exhaust duct, moved across the bottom, and then passed through the bioscrubber.

A schematic of the bioscrubber is shown in Fig. 2C. Contaminated exhaust air is introduced upwards from the bottom, passes through the layer of inorganic structured packing materials, and finally flow out from the outlet at the top. The packing was formed by stacks of coarse plastic square plate (polyethylene, 0.3 m in length and 1.0 cm in thickness). The distance of each plate was around 5 cm. The stack was vertical packing with 45° tilt to the airflow direction. Fresh water is simultaneously sprayed on top of the bioscrubber to keep the packing materials wet. Opposite flow directions of the exhaust air and fresh water (countercurrent) can provide intensive contact between air and water and enables the transformation of contaminated pollutants from gas phase to liquid phase. The moisture

Figure 2. (A) Scheme of mechanical ventilation channels inside the pig house, (B) photograph of the bioscrubber on the roof of a pig house, and (C) schematic diagram of the bioscrubber. BS indicates bioscrubber.

condition caused by the water spray can also promote bacterial growth and extend the contact time between bacteria and pollutants.

The characteristics of all bioscrubbers (BS1–BS13) are summarized in Table 1. The maximum inlet air ventilation rate (IAVR) of all the plants was higher than $13.9 \text{ m}^3 \text{ s}^{-1}$, and the ventilation rate of the plants at the sampling time were generally higher than $11 \text{ m}^3 \text{ s}^{-1}$. The empty bed air residence time (EBRT) ranged from 1.3 to 18.0 s. Although the layer volume of the packing materials varies from 17.5 to 100.4 m^3 , the packing thickness for each bioscrubber remains the same (1.8 m). The recirculation water spray rates were in a range of $3\text{--}30 \text{ m}^3 \text{ h}^{-1}$. Once the electrical conductivity (EC) of the recirculation water exceeds 22 mS cm^{-1} (around every 1–2 months), the water with half volume of each recirculation tank was discharged and fresh water was filled up.

2.2 Sampling and measurements

All bioscrubbers were built and operated for 1–7 years before the first sampling in 2013. The second sampling campaign was in 2015, 2 years later, to evaluate the performance stability of the bioscrubbers. In both 2013 and 2015, samples were collected for each bioscrubber in the same season, spring (May or June), at the temperature range of $16\text{--}24^\circ\text{C}$. Triplicate samples of gas and recirculation water in each site at each sampling time were taken and analyzed. Owing to problems with laboratory supplies in 2013, only gas samples were further analyzed, and NH_3 concentrations were only tested in eight bioscrubbers (BS1–BS8). In 2015, all gas and water samples were processed.

2.2.1 Exhaust air sample

An electric air pump (SP 750 EC/50 Hz, Schwarzer Precision, Germany) was used to sample exhaust air at the inlet and outlet for each bioscrubber. The pump airflow rate was around 6 L min^{-1} . For each sampling (triplicates sample for each sample type), one side of the pump was connected to the inlet or outlet gas channel of the bioscrubber, the other side was connected to a vacuum glass tubes (10 mL) equipped with single polypropylene fittings. Thus, the inlet/outlet gas of the bioscrubber statically passed through the tubes, and the tube was connected after the first 10 min gas discarded when the gas samples were assumed to be representative. The CH_4 , CO_2 , and N_2O concentrations were determined by a gas chromatograph (7890A, Agilent Technologies, USA). The injection volume was $250 \mu\text{L}$. Gases were separated on a Porapak Q column (1.8 m length, 2 mm ID) and quantified with a flame ionization detector (FID) for CH_4 and CO_2 , and an electron capture detector (ECD) for N_2O . The inlet, oven, and detector temperatures were 75, 35, 280 (FID), and 350°C (ECD), respectively. Helium served as the carrier gas (30 mL min^{-1}). The NH_3 concentration was measured in the inlet/outlet gas channel of the bioscrubber with Draeger gas detection tubes in site [12]. The concentration of the gases was reported as ppm and calculated to mg m^{-3} as follows: 1 ppm of NH_3 , CH_4 , N_2O , and CO_2 equals 0.70, 0.65, 1.80, and 1.80 mg m^{-3} , respectively, under default conditions of 20°C and 1 atm. NH_3 , CH_4 , N_2O , and CO_2 inlet loading rates were calculated

as Eq. (1). NH_3 and CH_4 removal efficiencies were calculated followed Eq. (2). N_2O and CO_2 production efficiency and production rate were calculated as Eqs. (3) and (4), respectively.

$$\text{Inlet loading rate (g d}^{-1}\text{m}^{-3}) = \frac{86,400 \times Q \times C_{in}}{1000 \times V} \quad (1)$$

$$\text{Removal efficiency (\%)} = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (2)$$

$$\text{Production efficiency (\%)} = \frac{C_{out} - C_{in}}{C_{in}} \times 100 \quad (3)$$

$$\text{Production rate (g d}^{-1}\text{m}^{-3}) = \frac{86,400 \times Q \times (C_{out} - C_{in})}{1000 \times V} \quad (4)$$

where Q is the corresponding inlet air ventilation rate ($\text{m}^3 \text{ s}^{-1}$), C_{in} is the corresponding inlet gas concentration (mg m^{-3}), and C_{out} is the corresponding outlet gas concentration (mg m^{-3}) of bioscrubbers. V is the packing material volume of bioscrubbers (m^3), 86,400 is the calculation factor to transfer second to day, and 1000 is the calculation factor to transfer mg to g.

Free NH_3 in the water solution was calculated using Eq. (5) reported by Baquerizo et al. [13]:

$$\text{FA} = \frac{(\text{NH}_4^+ - \text{N} \times 10^{\text{pH}} \times (17/14))}{(e^{6344/(273+T)} + 10^{\text{pH}})} \quad (5)$$

where FA is the free NH_3 concentration (mg L^{-1}), $\text{NH}_4^+ - \text{N}$ is the concentration of $\text{NH}_4^+ - \text{N}$ (mg L^{-1}), and T is the water temperature ($^\circ\text{C}$).

2.2.2 Recirculation water sample

At each sampling occasion in 2015, for each bioscrubber, approximate 1000 mL of each water sample (three samples in each site) from the recirculation buffer tank was collected in amber flasks (full volume). The pH, EC, and temperature were measured immediately in the field. The pH was measured by a pH meter (pH/Cond 340i, WTW, Germany), EC and temperature were measured by a potentiometer (Multi 350i, WTW, Germany). The remaining water samples were transported and cooled to the laboratory for ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) analysis within 24 h. NO_2^- and NO_3^- were measured using a high-performance liquid chromatograph (HPLC 1200 Series, Agilent Technologies, USA) equipped with a C-18 column (Hypersil ODS, $125 \times 4.0 \text{ mm}$, $5 \mu\text{m}$, Agilent Technologies, USA) and a UV detector (model 430) according to the description by Sanders et al. [14]. NH_4^+ concentration was determined by a photometer according to German standard methods (DIN 38406-E5-1).

2.2.3 Bacterial morphological properties

Biofilm samples from the packing material of selected bioscrubbers (BS1, 7, 8, 9, and 11) were collected to evaluate the morphological properties of the bacterial communities in 2015 one week after the gas samples analyzed. These bioscrubbers were selected

Table 1. Characteristics of the 13 tested field-scale bioscrubbers treating the exhaust air of pig houses

No.	Construct Year	Maximum IAVR ^{a)} (m ³ s ⁻¹)	IAVR ^{a)} at sampling time (m ³ s ⁻¹)	EBRT ^{b)} (s)	Packing material volume (m ³)	Recirculation water tank volume (m ³)	Recirculation water flow (m ³ h ⁻¹)
BS1	2009	38.9	28.3	2.1	59.6	21.5	10
BS2	2009	34.7	14.9	3.1	47.0	20.5	10
BS3	2011	27.6	13.8	3.2	44.1	55.0	20
BS4	2007	13.9	1.0	18.0	17.5	6.3	3
BS5	2006	27.8	16.4	2.2	35.9	13.1	5
BS6	2012	30.0	23.0	2.0	46.7	17.0	5
BS7	2011	39.1	23.5	2.4	57.0	70.0	30
BS8	2010	17.6	3.5	9.1	32.1	40.0	20
BS9	2009	23.6	13.2	2.8	36.3	13.0	5
BS10	2011	29.2	7.5	6.2	46.7	16.0	10
BS11	2010	66.7	30.7	3.3	100.4	36.3	15
BS12	2011	17.8	11.6	2.8	31.9	11.6	5
BS13	2012	66.7	24.6	1.3	33.0	43.1	20

^{a)}IAVR: Inlet air ventilation rate.

^{b)}EBRT: Empty bed air residence time; calculated as packing bulk volume (m³) divided by the maximum airflow rate (m³ s⁻¹).

to represent all investigated bioscrubbers due to their NH₃ and CH₄ removal efficiencies generally covered all the whole detected range. The preparation of biofilm samples followed the procedure described by Fiencke and Bock [15] and Spieck and Lipski [16]. Briefly, the biofilm samples for bacterial communities were fixed immediately in 2.5% glutaraldehyde after sampling. Packing materials were washed three times in cacodylate buffer (sodium salt, 75 mM) and embedded in a drop of 2% noble agar. Then, fixed samples were additionally examined with a transmission electron microscope (Leo 906E with a CCD camera model 794) at Biocenter Klein Flottbek, Universität Hamburg.

2.3 Statistical analysis

A linear regression test was used to determine the correlation between the inlet loading rate of NH₃ and CH₄, EC, and dissolved inorganic nitrogen (DIN) in the recirculation tank water samples. The simple linear regression tests were computed by the SPSS version 9.0 software (SPSS, Inc., Chicago, IL), and the Pearson coefficient was evaluated at the 5% level ($p < 0.05$).

3 Results and discussion

3.1 NH₃, N₂O, CH₄, and CO₂ treatment

Figure 3 shows the inlet loading rate and removal/production efficiency of the 13 bioscrubbers treat intensive pig houses exhaust air in 2013 and 2015. The NH₃ inlet loading rates varied between 34 and 755 g d⁻¹ m⁻³ in 2013 and in the similar range of 34 and 686 g d⁻¹ m⁻³ in 2015. The overall average NH₃ inlet loading rate was 268 g d⁻¹ m⁻³ in 2013 and 2015. NH₃ removal efficiencies varied between 35 and 100% with an overall average value of 79% under the NH₃ inlet fluctuations. The NH₃ removal efficiencies of bioscrubbers were also previously reported to range from 45 to 96% when treating pig house exhaust gas under different operating parameters [10, 17]. Moreover, when

comparing the NH₃ removal efficiency of the same bioscrubber in 2013 and 2015, the results achieved clear improvement in BS3, 4, 6, and 7 and maintained high removal efficiency (around 80%) in BS1, 2, and 4, with only one decreased value of BS8 in 2015. Thus, it can be expected that bioscrubber was a promising technology for NH₃ removal from intensive pig houses in northern Germany.

The N₂O inlet loading rates ranged from 3 g d⁻¹ m⁻³ to 87 g d⁻¹ m⁻³ in 2013 and 4 g d⁻¹ m⁻³ to 44 g d⁻¹ m⁻³ in 2015 with an overall average value of 26 g d⁻¹ m⁻³. The N₂O outlet concentration was higher than the inlet and shows 9–578% production efficiency compared with the inlet. It was reported by Melse and Mosquera [18] that NH₃ removed from the inlet air was not completely converted to N₂ but also to N₂O, in biotrickling filters (bioscrubbers) used for NH₃ removal at livestock facilities. It supported that, in the present study, a part of NH₃ inlet (approximate 6% in 2013 and 4% in 2015) was converted to N₂O during the NH₃ removal process in the 13 bioscrubbers.

CH₄ inlet loading rates of the bioscrubbers varied from 491 to 6489 g d⁻¹ m⁻³ with an overall average of 1809 g d⁻¹ m⁻³ in 2013 and 2015. For CH₄ removal, some of the bioscrubbers could reduce 22–35% (BS 1, 6, 11, and 13) and 21–63% (BS 1, 2, 4, 5, 8, and 11) of the inlet CH₄ as measured in 2013 and 2015, respectively. However, majority of the bioscrubbers did not show CH₄ reduction. Even though CH₄ removal efficiencies had a big range (–142 to 60%), most of the CH₄ removal efficiencies were in the range from –10 to 20% with an overall average value of –1% which indicated CH₄ is hard to remove in the bioscrubbers. Previous studies have demonstrated that CH₄ was not affected by the bioscrubbers treatment [8, 9]. It may be due to CH₄, which is a scarcely water-soluble component, and the EBRTs in the present study (1.3–18.0 s) is insufficient to transfer CH₄ from the gas phase to the liquid phase and then further degrade in the bioscrubbers [19].

For CO₂, inlet loading rates varied from 19×10^3 to 316×10^3 g d⁻¹ m⁻³ and the overall average CO₂ production was around zero in 2013 and 2015. CO₂ production could be interpreted as the result of the CH₄ oxidation process or an endogenous

Figure 3. Inlet loading rate of exhaust air (NH_3 , N_2O , CH_4 , and CO_2), removal (for NH_3 and CH_4), and production (for N_2O and CO_2) efficiencies from 13 selected bioscrubbers in 2013 and 2015. Error bars of values for 2015 represent the standard variation ($n=3$). A dotted line in each plot represents the average value for corresponding parameters.

Figure 4. Interaction of exhaust air treatment and water parameters from 13 selected bioscrubbers in 2013 and 2015: (A) NH₃ versus CH₄ inlet loading rate, (B) NH₃ inlet loading rate versus NH₃ reduction rate, (C) NH₃ removal efficiency and NH₄⁺-N concentration versus pH of bioscrubbers' recirculation water samples in 2015, (D) EC versus DIN compounds of bioscrubbers' recirculation water samples in 2015. A solid line represents the linear regression analysis result. A dotted line represents the correlation tendency of both parameters.

respiration by other microbial population during the biological technique treatment [20]. Thus, hardly removal capability of CH₄ in the bioscrubbers may support the low CO₂ production in the present study.

3.2 Interaction of exhaust air treatment

As can be seen from Fig. 4A, a linear relationship ($R^2 = 0.51$) was found between the CH₄ and NH₃ inlet loading rates. The reason might be the dependence of all CH₄ and NH₃ emissions on the same factors, such as animal species and numbers, weight and age, composition of the animal feed, type of animal housing, and manure storage [21].

NH₃ inlet loading rates versus NH₃ reduction rates for all bioscrubbers in both 2013 and 2015 are shown in Fig. 4B. The reaction rate of NH₃ could be simplified to the zero-order kinetics ($R^2 = 0.71$) with a reaction rate limitation of 395 g d⁻¹ m⁻³ under the NH₃ loading rate of 401 g d⁻¹ m⁻³. NH₃ reduction rates seem to slow down, when the NH₃ loading rate was higher than 401 g d⁻¹ m⁻³. However, there is only two data points that need to be further investigated to make a conclusion.

3.3 Recirculation water parameters

Table 2 shows the pH, temperature, EC, NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N concentrations in the recirculation water samples of

the 13 bioscrubbers measured in 2015. The recirculation water temperature varied between 14.8 and 21.5°C during the sampling time. The pH values were observed between 6.1 and 8.1, and EC values ranged from 6.4 to 20.4 mS cm⁻¹. NH₄⁺-N concentrations in recirculation water were detected in the range of 0.20–2.56 g L⁻¹. Moreover, NO₂⁻-N concentration (0.18–2.11 g L⁻¹) was generally clearly higher than the corresponding NO₃⁻-N concentration (0.04–0.76 g L⁻¹) in the recirculation water sample for each bioscrubber.

The presence of NO₂⁻-N and NO₃⁻-N in recirculation water was produced mainly due to the nitrification process after inlet NH₃ dissolved in the water. The higher level of NO₂⁻-N concentration than NO₃⁻-N concentration may be caused by inhibition of NO₂⁻-N oxidation during nitrification (Fig. 1A). Previous research revealed that free NH₃ accumulation in water can promote this inhibition; the high concentration of free NH₃ greatly inhibits the conversion of NO₂⁻-N to NO₃⁻-N than that of NH₃-N to NO₂⁻-N [13]. On the basis of Eq. (5), free NH₃ concentration in the recirculation water of the studied bioscrubbers was between 0.3 and 93.4 mg L⁻¹, a range that was determined to cause nitrification inhibition (threshold of 0.1 mg L⁻¹), especially for the oxidation process from NO₂⁻-N to NO₃⁻-N [13]. This effect could well explain why the concentrations of NO₂⁻-N were much higher than those of NO₃⁻-N for the bioscrubbers, as shown in Table 2.

In Fig. 4C, NH₄⁺-N concentration in the recirculation water samples shows a positive correlation tendency with pH (in the range of 6.1–8.1) in the present study; however, the NH₄⁺-N

Table 2. Main characteristics of recirculation water for 13 field-scale bioscrubbers in 2015

No.	pH	water temperature (°C)	Electrical conductivity (mS cm ⁻¹)	NH ₄ ⁺ -N (g L ⁻¹)	NO ₂ ⁻ -N (g L ⁻¹)	NO ₃ ⁻ -N (g L ⁻¹)
BS1	6.7 ± 0.1	14.9 ± 0.1	6.4 ± 0.1	0.20 ± 0.01	0.18 ± 0.02	0.04 ± 0.00
BS2	6.7 ± 0.3	14.8 ± 0.1	8.6 ± 0.2	1.02 ± 0.01	0.23 ± 0.01	0.70 ± 0.02
BS3	7.1 ± 0.1	19.2 ± 0.2	18.5 ± 0.2	2.04 ± 0.06	1.44 ± 0.01	0.37 ± 0.01
BS4	6.1 ± 0.2	21.5 ± 0.1	16.9 ± 0.1	1.22 ± 0.03	1.68 ± 0.01	0.14 ± 0.01
BS5	6.8 ± 0.2	19.3 ± 0.3	19.9 ± 0.1	2.58 ± 0.05	2.11 ± 0.01	0.07 ± 0.01
BS6	7.6 ± 0.2	17.8 ± 0.2	19.0 ± 0.1	2.33 ± 0.03	0.24 ± 0.02	0.76 ± 0.01
BS7	7.5 ± 0.1	19.0 ± 0.2	16.0 ± 0.1	1.72 ± 0.01	0.84 ± 0.01	0.16 ± 0.02
BS8	8.1 ± 0.2	17.6 ± 0.2	19.5 ± 0.2	1.92 ± 0.02	1.07 ± 0.01	0.26 ± 0.01
BS9	6.9 ± 0.1	20.5 ± 0.1	14.5 ± 0.1	1.54 ± 0.03	1.75 ± 0.02	0.06 ± 0.01
BS10	6.7 ± 0.1	20.5 ± 0.2	20.4 ± 0.1	2.22 ± 0.02	1.88 ± 0.02	0.21 ± 0.02
BS11	7.1 ± 0.1	16.0 ± 0.3	19.2 ± 0.2	2.52 ± 0.02	1.47 ± 0.01	0.42 ± 0.02
BS12	7.2 ± 0.2	17.5 ± 0.3	18.6 ± 0.2	2.56 ± 0.02	1.54 ± 0.02	0.42 ± 0.01
BS13	7.6 ± 0.1	20.3 ± 0.2	20.1 ± 0.1	2.14 ± 0.02	1.79 ± 0.01	0.14 ± 0.01

Figure 5. Scanned electron micrographs of (A) NH₃ oxidizers and (B) CH₄ oxidizers from bioscrubber plants in 2015 by transmission electron microscopy. Abbreviations: ICM, intracytoplasmic membrane; R, ribosomes; PHB, poly-β-hydroxybutyrate.

concentration seems to be stable when pH is above 7. This finding could be attributed to the lower pH making it much easier for NH_3 dissolved into water and increase the pH value by producing NH_4^+ -N until the saturation point. NH_3 achieved higher (>79%) removal efficiencies when pH values lower than 7, which suggested lower pH values, with the range of 6.1–7 in the present study, of the recirculation water may benefit NH_3 removal due to the dissolution of NH_3 in the bioscrubbers' recirculation water.

EC values of the recirculation water were reportedly influenced mainly by the dissolved nitrogen compounds, e.g. NH_4^+ -N, NO_2^- -N, and NO_3^- -N, and in the Netherlands and Belgium, it is obligated to measure EC in bioscrubbers because it can give an indication for the amount of dissolved nitrogen and rapidly diagnose bioscrubbers' performance [10]. In the present study, EC values ranged from 6.4 to 20.4 mS cm^{-1} . The sum of the NH_4^+ -N, NO_2^- -N, and NO_3^- -N concentrations for each sample is plotted versus the corresponding EC values in Fig. 4D, which shows a significantly positive correlation, with the equation of $Y_{\text{DIN}} = 0.25X_{\text{EC}} - 0.80$ ($R^2 = 0.83$). It demonstrated the performance stability of the selected 13 field applied bioscrubbers in northern Germany.

3.4 Morphological properties of NH_3 and CH_4 oxidizers

Transmission electron microscopy (TEM) technology was used to detect the respective bacterial morphological properties (e.g. cell shape, intracytoplasmic membrane (ICM) distribution and structure) of the NH_3 (Fig. 5A) and CH_4 oxidizers (Fig. 5B) from BS 1, 7, 8, 9, and 11. These bioscrubbers were chosen to generally represent the full range of NH_3 (35–100%) and CH_4 (–69% to 35%) removal efficiencies for all investigated bioscrubbers.

For NH_3 -oxidizing bacteria, on the basis of their phenotypic characteristics, five species, *Nitrosomonas*, *Nitrosococcus*, *Nitrosolobus*, *Nitrospira*, and *Nitrosovibrio*, were primarily distinguished by cell shape and specific arrangement of ICM when TEM technology was used [22, 23]. As shown in Fig. 5A, *Nitrosomonas* sp. was the most probable bacterial species detected, which was verified in all tested bioscrubbers. The observed bacterial species showed densely stacked ICM arranged in the peripheral cytoplasm and mainly rod-shaped cells surrounded by a slime layer. In the examined biofilm samples, no other significant spherical NH_3 -oxidizing bacterial cells were detected. Moreover, higher density bacterial cell number and ICM-related membrane structures were observed via electron microscopy for BS 1, 9, and 11 (NH_3 removal rates of 100, 100, and 73%, respectively) than those for BS 7 and 8 (NH_3 removal rates of 50 and 35%, respectively). *Nitrosomonas* sp. was demonstrated to be a major NH_3 oxidizer in the first step of the nitrification process for waste gas treatment by various bioreactors, such as biofilters and bioscrubbers [24, 25]. The ICM structure of *Nitrosomonas* sp. may also play an important role in nitrification transformation because of the high concentration of membrane-bound metal proteins, such as ammonia monooxygenase, which is the key enzyme of NH_3 oxidation and cytochromes [15, 26].

For CH_4 -oxidizing bacteria, methanotrophs can be divided into three groups (types I, II, and X) by multiple criteria, including cell morphology, ICM structures, and some physiological characteristics: type I includes the genera *Methylomonas* and *Methylobacter*, type II includes the genera *Methylosinus* and *Methylocystis*, and type X includes the genus *Methylococcus* [27, 28]. The short rod-shaped cells of type I methanotrophs possess ICM in bundles distributed throughout the cells, whereas the crescent-shaped rods and pear-shaped cells of type II methanotroph species are characterized by paired membranes distributed along the periphery of the cells. As shown in Fig. 5B, typical type I methanotrophs, membranes were centrally arranged as flat sheets/lamellar stacks in bacteria [29], were most probably found in BS plants 1, 8, 9, and 11 (CH_4 removal efficiencies of 23, 28, 3, and 63%, respectively) but not in BS7 (CH_4 removal efficiencies of –69%). It demonstrated for the first time that type I methanotrophic bacteria exist, which may contribute to CH_4 removal in field-scale bioscrubbers when treating exhaust air from pig houses.

4 Concluding remarks

The 13 selected bioscrubbers' performance of treating exhaust gas emission of NH_3 and the greenhouse gases CH_4 , N_2O , and CO_2 from intensive pig production houses in northern Germany was investigated in 2013 and 2015. The results showed that all bioscrubbers presented overall average of 79% NH_3 removal efficiencies, which varied between 35 and 100% under the NH_3 inlet fluctuations in both 2013 and 2015. *Nitrosomonas* sp. and type I methanotrophs were demonstrated to be the dominant NH_3 - and CH_4 -oxidizing bacteria in bioscrubbers, respectively. However, overall average removal efficiency of CH_4 was approximately zero, indicating that CH_4 was hard to remove from bioscrubbers in normal operation. EC effectively indicated DIN concentration, which demonstrate the stable performance of the 13 selected field-scale bioscrubbers.

Practical application

Bioscrubbers, as a robust, sustainable, and low-cost technology, showed a clear increasing tendency for pig house exhaust gas emission treatment; however, the exhaust air treatment reliable assessment and relative pollutants removal mechanisms have not yet been fully studied. The present study is the first original research paper regarding to the performance assessment of field-scale bioscrubbers in northern Germany, one of the biggest pig production area in the world. The results showed that all bioscrubbers presented overall average of 79% NH_3 removal efficiencies under the NH_3 inlet fluctuations in both 2013 and 2015, which confirms that field-scale bioscrubber is a promising technology for NH_3 removal from intensive pig house in northern Germany. Moreover, *Nitrosomonas* sp. and type I methanotrophs were first time demonstrated to be the dominant NH_3 - and CH_4 -oxidizing bacteria, respectively, in bioscrubbers by electron microscopy technology.

The authors express their sincere acknowledgements to Christian Radau from RIMU Agrartechnologie GmbH for his technical assistance. This work was financially supported by the German Federal Ministry of Education and Research (BMBF), the Beijing Commission of Science and Technology (D151100005115004), and the China Scholarship Council.

The authors have declared no conflict of interest.

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