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Possible environmental applications of a recently developed ammonia isotope monitoring photoacoustic system

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Abstract— Ammonia is one of the most significant environmental pollutants. Concentration measurements, identifying the sources and studying the transformations in the biosphere are essential, and they are the focus of many investigations. The near-infrared (≈1530 nm) photoacoustic method for simultaneous and selective determination of $^{14}NH_3$/$^{15}NH_3$ isotopologues reported here can be suitable for monitoring these phenomena and processes. So far, the photoacoustic method has not been used for this kind of examination. The application of our measurement method makes it possible to eliminate the disadvantages of the previous measurement methods. The detection limit of the PA system is 0.14 ppm and 0.73 ppm for $^{14}NH_3$ and $^{15}NH_3$, respectively, which can be improved by orders of magnitude with further development of sampling and measurement techniques.

Key-words: atmospheric ammonia, isotopologues of ammonia, isotope abundance of $^{15}NH_3$, ammonia concertation, isotope tracer, isotope labelling, photoacoustic method for ammonia, near-infrared spectroscopy

1. Introduction

Nowadays, one of the most serious environmental risks is the accumulation of reactive nitrogen in different spheres of the Earth. Since the beginning of the last century, the *Haber-Bosch* ammonia synthesis converts a great amount of inert N_2 into NH_3 first of all for fertilizer production. The global NH_3 production is about 175 million tons per year and is expected to increase by 3–5% per year in the future (*Wang et al.*, 2021). It is estimated that the efficiency of applied N is less than 50 and 70% under tropical conditions and temperate regions, respectively (*Baligar* and *Bennett*, 1986; *Malhli* and *Nyborg*, 1991; 1992; *Malhi et al.*, 2001). Losses of N are mainly due to leaching, runoff, and volatile losses of ammonia. Further losses occur during harvesting, food processing, trading, and consumption. Finally, all the nitrogen content of fertilizers enters the environment, accumulating yearly in various spheres.

Circulation of anthropogenic nitrogen in Earth's atmosphere, hydrosphere, and biosphere has a wide variety of consequences, causing multiple effects in the atmosphere, in terrestrial ecosystems, in freshwater and marine systems, and on human health. This sequence of effects is called nitrogen cascade (*Galloway et al.*, 2003). The harmful effects of reactive nitrogen can be traced in the deterioration of water quality (eutrophication), the impact on air quality (visibility, $PM_{2.5}$, smog), the reduction of biodiversity, the acidification of soil and groundwater, the increase of the greenhouse effect, and the decomposition of stratospheric ozone by N_2O.

Since ammonia plays a prominent role in the nitrogen cascade, the investigation of the atmospheric concentration and the exchange of NH_3 gas between the atmosphere and the surface has been among the main research goals of the last decades.

Investigation of the concentration ratio of stable ammonia isotopes ($^{14}NH_3$ and $^{15}NH_3$) is a good tool to monitor the exchange and transformation processes. There are two stable isotopes of nitrogen, ^{14}N and ^{15}N. Their molar ratio in atmospheric N_2 is 0.99636/0.00364, i.e., the volume ratio of ^{15}N is 0.3653%. The isotope abundance in the inert atmospheric N_2 is regarded as the standard in the calculation of isotope abundance of ^{15}N, however, this ratio changes due to the fractionation. All of the physical and chemical processes are accompanied by the change in the isotope abundance of $^{15}NH_3$. With the determination of the abundance of $^{15}NH_3$ ($\delta^{15}N$-NH_3) we can qualify and quantify the ammonia emission sources (*Bhattarai et al.*, 2021; *Elliott et al.*, 2019; *Felix et al.,* 2013;2017; *Wang et al.*, 2022).

Isotope labelling is another frequently used method in environmental investigations. Since ^{15}N-enriched N compounds became commercially available in the 1970s, the number of applications of the stable isotope to study soil processes rapidly increased, taking advantage of the phenomenon that biological processes prefer the lighter ^{14}N isotope, i.e., the products of the processes contain less ^{15}N, as before the processes (i.e., $\delta^{15}N$ decreases) (*Nômmik* et al., 1973; *Sánchez*, 2001; *Zhao et al.*, 2016). The addition of a ^{15}N tracer to follow the catalytic reduction of nitric oxide to ammonia is also a frequently used method (*Ettireddi et al.*, 2012; *Ozkan et al.*, 1994).

There are several methods to determine the concentration of atmospheric ammonia. During the concentration measurement selectivity, sensibility, response time, and minimum detectable concentration are the most critical parameters. A general disadvantage of the measurement of ammonia gas is the adsorption on the surface of the sampling device or the walls of the sensor cell resulting in bias during the measurement. Some of the procedures are based on physical methods like spectroscopy (*Bobrutzky et al.*, 2010; *Dang et al.*, 2019; *Gall et al.*, 1991; *Huszár et al.*, 2008; *Pushkarsky et al.*, 2002; *Schilt et al.*, 2004), spectrometry (*Martin et al.*, 2016; *Norman et al.*, 2007; 2009; *Nowak et al.*, 2006; 2007; *Vasileiou et al.*, 2015a; 2015b; 2016), or fluorometry (*Amornthammarong et al.*, 2011; *Kéruel* and *Aminot*, 1997). The chemical methods are mostly based on the transformation of ammonia gas into ammonium ion in the aquous phase, followed by the determination of ammonium (*Allegrini et al.*, 1987; *ASTM*, 2015; *EMEP*, 1996; *Erisman et al.*, 2001; *Jeong et al.*, 2013; *Koroleff*, 1970; *Thomas et al.*, 1973; 2002; *Rice et al.*, 2012).

Separated simultaneous measurement of $^{14}NH_3$ and $^{15}NH_3$ isotopologues of ammonia gas can mostly be achieved by physical methods (*Phillips et al.*, 2018; *Chang et al.*, 2016; 2019; *Griffiths* and *de Haseth*, 2007; *Felix et al.*, 2017; *Koletzko et al.*, 1995; *Lee et al.*, 2011; 2014; *Lehmann*, 2017; *Liu et al.*, 2020; *McEnaney et al.*, 2017; *Murakami et al.*, 2005; *Nielander et al.*, 2019; *Nômmik*, 1973; *Simonova* and *Kalashnikova*, 2019; *Taghizadeh-Toosi et al.*, 2012; *Tonn et al.*, 2019; *Wang et al.*, 2017; *Wu et al.*, 2019; *Zhao et al.*, 2016).

So far, the employed analytical methods, especially in spectroscopy, are either very expensive, need large sensing volumes (NMR: Nuclear magnetic resonance method), have uncertainties at very low NH_3 concentrations (IRMS: isotope ratio mass spectroscopy), or are limited by the availability of the tunable laser light at the appropriate wavelength (CRDS: cavity ring-down spectroscopy), or simply have a problem in the control of its background signal (CIMS: chemical ionization mass spectroscopy).

Most of the analytical methods are not continuous, were done by active or passive sampling, and the evaluation is complicated. One exception is the method of *Phillips et al.* (2018) where the optical path length is of the order of 10 m through a generated plume making its application in the laboratory impossible.

To the best of the authors' knowledge, photoacoustic method has not been used for the simultaneous measurement of ammonia isotopes. The aim of our work has been to develop a simple, reliable, automatic, and robust system for the selective, rapid, and sensitive measurement of ammonia isotopes by using a near-infrared photoacoustic (NIR-PA) system.

Moreover, to achieve the above aim, there was a need for methodological development, construction of the measuring instruments, and finally, development of gas sampling procedures to be used. The following sub-aims were therefore carried out:

- Design and construction of a NIR-PA system capable of selectively measuring and differentiating between ammonia gas isotopes ($^{14}NH_3$ and $^{15}NH_3$).
- Selection and optimization of the measurement and modulation parameters (wavelength, laser operating temperature, etc.).
- Construction, testing, and calibration of the newly developed NIR-PA system.
- Solving the incidental problems and improvement of the system by re-optimization of the selected parameters.
- Evaluation of the developed NIR-PA system.

2. Experimental

2.1. Instrumentation set-up

The measurement system consisted of two main parts. A photoacoustic detection unit for concentration measurement, employing two types of diode lasers (an external cavity diode laser and a telecommunication type fiber coupled Near Infrared DFB diode laser), together with integrated electronics. The electronic's main purpose was to amplify, provide temporal averaging, filter the microphone signal, control the temperatures of the laser and the detection cell, and feed the modulated driving current to the diode laser.

The second part consisted of ammonia isotopes gas generating units which were of two types; NH_3 in N_2 cylinder (1000 ppm ± 1%, with a purity of 5.0) supplied by the Hungarian Messer company) and a chemical reaction-NH_3 generation-based mode. For more details, refer to *Ouma et al.* (2022).

2.2. Spectral measurements and analytical parameters

The $^{14}NH_3$ and $^{15}NH_3$ spectra were recorded using two DFB diode lasers separately, with the same modulation parameters as shown in *Fig. 1.* The wavelength modulation (WM) was used during the measurements due to its improved sensitivity and noise-rejection capabilities over amplitude modulation. The WM spectrum is a derivative form of the absorption spectrum.

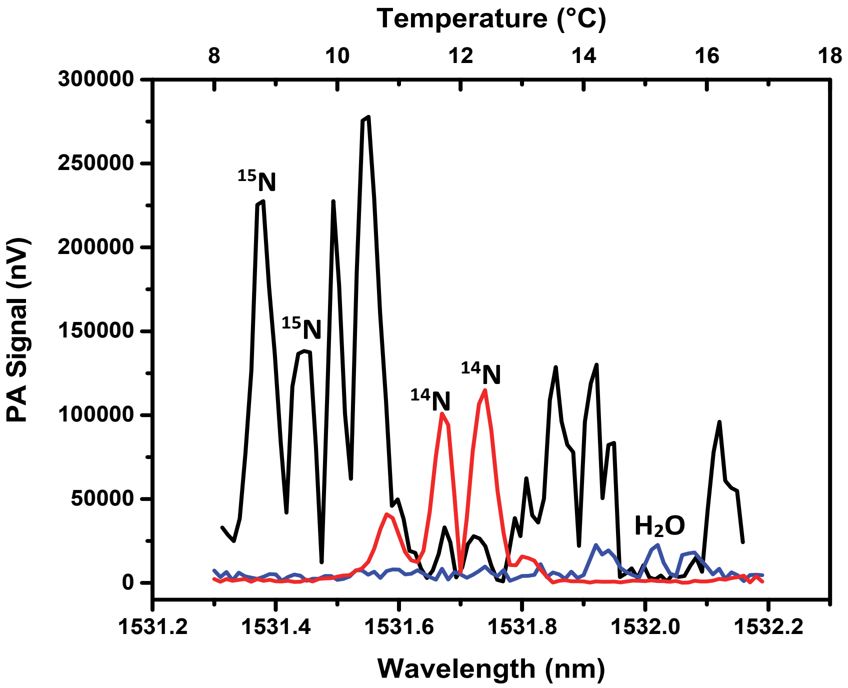

Fig 1. PA spectra of the ammonia isotopes; 600 ppm $^{15}NH_3$ (black line) and 95 ppm $^{14}NH_3$ (red line) as recorded by DFB diode laser. Cross-sensitivity spectrum of 5% water vapor (blue line) is also shown.

To minimize the cross-sensitivity and the disturbing effect of water vapor, four peak wavelengths, two for each isotope as shown in *Fig. 1*, were selected for the calibration measurements. Using two-two wavelengths for each isotope reduces the cross-sensitivity and increases the sensitivity of the method.

Calibration of the ammonia isotopes was then done using both the cylinders and the chemical reaction NH_3 generation methods. Measurement of the photoacoustic signal (PAS) in the function of volume mixing ratio (VMR) was performed in the range of 0–1000 ppm. The cross-sensitivity between the two isotopes measured simultaneously, calculated calibration lines, and the slope of the calibration line in nV/ppm which corresponded to the sensitivity of the NIR-PA system are all given in *Table 1*. For more technical details, refer to *Ouma et al.* (2022).

Table 1. Summary of the analytical parameters of the newly developed NIR-PA system (PAS: photoacoustic signal; VMR: volume mixing ratio)

Parameters	**Values obtained**
Modulation current (mA)	AC/DC: 10 /146
Modulation temperature (°C)	Laser 1: 18.10 °C and 18.69 °C for $^{14}NH_3$ 8.65 °C and 9.45 °C for $^{15}NH_3$ Laser 2: 20.95 °C and 21.56 °C for $^{14}NH_3$ 11.77 °C and 12.36 °C for $^{15}NH_3$
Measurement wavelengths (nm)	$^{14}NH_3$: 1531.66 and 1531.73 $^{15}NH_3$: 1531.37 and 1531.45
Cross-sensitivity (nV/ppm)	$^{14}NH_3$: -1.3×10^{-4} $^{15}NH_3$: 7.4×10^{-3}
Cross-sensitivity bias	$^{14}NH_3$: –0.002% $^{15}NH_3$: 0.57%
Calculated calibration lines	$^{14}NH_3$: PAS (μV) = $6.61\times VMR$ (ppm) $^{15}NH_3$: PAS (μV) = $1.3\times VMR$ (ppm)
Detection limit (ppm)	$^{14}NH_3$: 0.14 $^{15}NH_3$: 0.73
System response time (s)	3.5

3. Possible applications for atmospheric measurements

3.1. Application of ^{15}N as tracer during electrochemical ammonia synthesis

There is an alternative way for the high energy-intensive and CO_2 emitter *Haber-Bosch* ammonia synthesis, the electrocatalytic reduction of N_2 into ammonia (see e.g., *Qing et al.*, 2020). This method, although still in the research and developmental stage, has shown great potential and is deemed less polluting and environmentally sustainable. While the process has produced promising results, several problems have been identified like its low efficiency (0.1–8%) and inaccuracy in the assessment of NH_3 levels produced. The latter problem is mostly due to the inability of the current NH_3 detecting equipment and analytical methods to reliably measure the low NH_3 gas produced (sub-ppm levels) without interference from common contaminants, such as human breath, laboratory air, contaminants in N_2 gas sources used in the synthesis process, etc.

3.2. Application of ^{15}N tracer in environmental analyses

There are lots of possible applications of the isotope tracer technique accompanied by photoacoustic detection, mostly in the investigation of soil biology and plant physiology processes. The nitrogen loss in form of ammonia can be estimated by the application of ^{15}N labeled fertilizer (e.g., *Nômmik*, 1973; *Zhao et al.*, 2016).

The transformation of soil N, like denitrification or the N fixation by plants, can also be traced by this technique (*Sánches*, 2001).

3.3. Application in source apportionment of atmospheric ammonia

As it was mentioned in the introduction, the reference abundance of ^{15}N (0.3653%) is changing in each physical and chemical process of ammonia due to the fractionation. The change in abundance ($\delta^{15}NH_3$, ‰), i.e., the source signature is representative of the given physical and chemical process. Identifying the ammonia source (e.g., agricultural or fossil fuel combustion process, industry, heating, traffic) by nitrogen isotope helps in designing a mitigation strategy for policymakers, but the existing methods have not been well validated (*Pan et al.*, 2020). The study of *Bhattarai et al.* (2020) highlights that collecting representative samples remains a challenge in fingerprinting $\delta^{15}N(NH_3)$ values of NH_3 emission sources, i.e., during the sampling, the isotope abundance changes compared to that of the representative for the given process. Since the application of PA systems does not need any sampling procedure the error caused by sampling and subsequent laboratory preparation can be avoided.

Because of the low abundance of $^{15}NH_3$, the source apportionment without the addition of a ^{15}N tracer requires a detection limit lower by orders of magnitude than it is reported in this paper. It can be achieved by the modification of the photoacoustic system described here by replacing the light source with a quantum cascade laser (QCL). Another possibility to improve the detection limit is the use of preconcentration sampling similarly to the method reported by *Pogány et al.* (2009).

4. Conclusion

This work has shown that measurement of ammonia isotopes ($^{14}NH_3$ and $^{15}NH_3$) using a photoacoustic measuring system fitted with a near-infrared diode laser light source around the wavelengths of 1532 nm is possible. Both NH_3 isotopes recorded strong absorption lines at this particular wavelength, while the values of their minimum detectable concentrations were 0.14 ppm for $^{14}NH_3$ and 0.73 ppm for $^{15}NH_3$. Due to the developed NIR-PA systems' robustness, high sensitivity, low cross-sensitivity, and short response time, it is expected to find a practical application in the detection and measurement of isotopically labeled NH_3 gas during the electrochemical synthesis process, as well as in the isotope tracer or source apportionment experiments.

Application of the photoacoustic method in these fields is a novelty and enables the elimination of the disadvantages of the previously used measurement techniques (high cost, complicated sampling, laboratory preparation, the error caused by sampling when measuring fractionalization, etc.). Fast response time is also an advantage in contrast to most of the previous measurement methods.

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