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Review

Analytical techniques for measuring nitrous oxide ☆

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ABSTRACT

Nitrous oxide (N_2O) is estimated to contribute about 6% of the global warming effect due to greenhouse gases. N_2O is also predicted to be the single most important ozone-depleting emission in the twenty-first century. Great progress has been made in N_2O measurement, but there is a critical need for sensors that can be used to map the spatial variation of N_2O emissions over a wide area. In this article, we outline where N_2O measurement is required, describe advances that have been made in developing sensitive analytical techniques and review some promising new technologies. Our aim is to assist both those new to N_2O measurement, enabling them to select the most appropriate of the available technology, and to inform those developing new analytical techniques.

Contents

1. Introduction . . . 66
2. Methods for measuring nitrous oxide . . . 67
 2.1. Sampling methods . . . 67
  2.1.1. Chamber methods . . . 67
  2.1.2. Micrometeorological methods . . . 67
3. Analytical techniques currently used . . . 68
 3.1. Chromatographic techniques . . . 68
 3.2. Optical techniques . . . 69
  3.2.1. Fourier-transform infrared spectroscopy . . . 69
  3.2.2. Infrared laser-absorption spectroscopy . . . 69
  3.2.3. Multipass cells . . . 70
  3.2.4. High-finesse optical cavities . . . 70
  3.2.5. Photoacoustic (PA) trace-gas detection . . . 70
 3.3. Amperometric methods . . . 71
4. New methods under development . . . 71
 4.1. Amperometric biosensors . . . 71
 4.2. Optical fibers . . . 71
 4.3. Modified-SnO_2 surfaces . . . 71
5. Conclusions . . . 71
 Acknowledgements . . . 71
 References . . . 71

Abbreviations: ECD, Electron-capture detector; QCL, Quantum-cascade laser; CRDS, Cavity ring-down spectroscopy; OA-ICOS, Off-axis integrated cavity-output spectroscopy; IRMS, Isotope-ratio mass spectrometry; PAS, Photoacoustic spectroscopy.

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1. Introduction

Nitrous oxide (N_2O) is a powerful greenhouse gas. The global warming potential (GWP) of N_2O is 298 times greater than CO_2 over a 100-year time horizon, and N_2O is estimated to contribute about 6% of the global warming effect due to greenhouse gases [1,2] In the stratosphere, N_2O is oxidized to form NO and NO_2. These nitrogen oxides catalyze the destruction of ozone [3], making N_2O the single most important ozone-depleting emission in the twenty-first century [4].

N_2O is an intermediate in both bacterial nitrification and denitrification pathways, so N_2O emissions are mainly due to bacterial transformations of nitrogen in soils and oceans (see Figs. 1 and 2). Since the industrial revolution (1750 AD), N_2O levels have increased by almost 20%, from 270 ppb to 320 ppb. This increase is attributed to human activities, in particular, the use of synthetic and organic fertilizers. Other important sources of N_2O emissions are human sewage and the burning of biomass and biofuels [5–7].

Under the Kyoto Protocol, signatory countries are required to complete an annual national greenhouse-gas inventory, which, for completeness, should include N_2O. Calculating N_2O emissions is a complicated task. In addition to N_2O emissions from agriculture, there are indirect emissions, such as those caused by leaching of nitrogen from agricultural fields to aquatic systems, which increase N_2O emissions from rivers and estuaries [8,9]. Furthermore, natural systems can act as important sources and sinks of N_2O [10]. The Intergovernmental Panel on Climate Change (IPCC) has set out guidelines for developing national greenhouse-gas inventories [11], whereby N_2O emissions are determined from models that link emissions to activities, such as fertilizer use. Underlying the models are emission factors, which are determined from experimental data. The accuracy of the models depends on the quality of the experimental data on which they are based [10,12].

Measuring N_2O emissions experimentally is not a trivial matter. Two main challenges are encountered when trying to measure N_2O emissions:

- first, the low atmospheric concentrations of N_2O (320 ppb), roughly a thousand times lower than CO_2, and these low concentrations are outside the detection range of many analytical techniques; and,
- second, N_2O fluxes are episodic and demonstrate very large temporal and spatial variations, due to the multiple processes that both produce and consume N_2O. The rates of these processes are affected by a wide range of factors, such as temperature, soil pH, moisture and soil organic carbon. While capturing flux events is challenging, it is critical to allow for accurate quantification of ecosystem-wide emissions [13,14].

A large amount of research is being carried out on N_2O fluxes from soils, wastewater and aquatic systems. This research aims not only to improve greenhouse-gas accounting, but also to understand the complex processes contributing to N_2O fluxes, which could be used to inform mitigation strategies.

Not only has the quantity of N_2O emissions been measured, but isotopic studies have also been performed, and have provided important information about the biogeochemical cycle of N_2O [15–19]. Although $^{14}N^{14}N^{16}O$ is the most abundant species (99%), both the ratio of $^{15}N/^{14}N$ and the position of ^{15}N (either $^{15}N^{14}N^{16}O$ or $^{14}N^{15}N^{16}O$) provide useful information [20–23]. Photolytic decomposition of N_2–O in the stratosphere, the major sink of N_2O, leads to enrichment of the heavier isotopes of N_2O (both ^{15}N and ^{18}O) [24,25]. Microbial sources generally emit N_2O that is depleted in ^{15}N and ^{18}O, while site preference ($^{15}N^{14}N^{16}O$ or $^{14}N^{15}N^{16}O$) can indicated whether N_2O is produced by nitrifying or denitrifying bacteria (see Fig. 2) [20,22,26].

To assist these studies, there is a strong need for better analytical methods and cost-effective ways of measuring N_2O over wide areas and long time-frames. The World Meteorological Organization Global Atmosphere Watch (WMO-GAW) guidelines for the measurement of N_2O recommend accuracy and precision of less

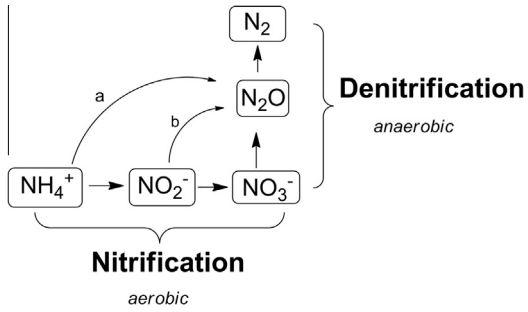

Fig. 2. Microbial pathways of N_2O production. (a) N_2O production through nitrification *via* hydroxylamine. (b) N_2O production through nitrifier denitrification. Figure modified from [19].

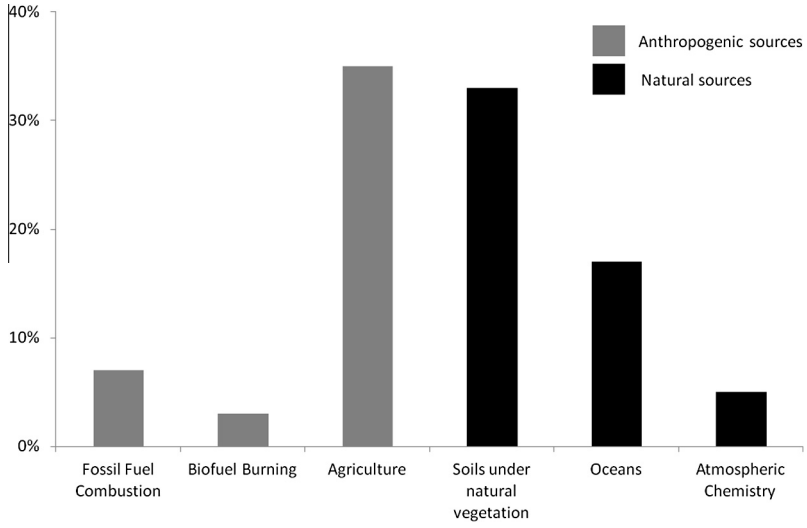

Fig. 1. Global sources of N_2O for the 1990s. Data for the graph was obtained from [5].