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Novel use of soil moisture samplers for studies on anaerobic ammonium fluxes across lake sediment–water interfaces

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Abstract

Small soil suction samplers have been used for several years to sample soil solution for chemical analysis in laboratory and glasshouse experiments. They are very cheap, effective and convenient. Here we describe for the first time their use in studies on sediment porewater. Bulk sediment from West Lake, a shallow hypereutrophic lake in Hangzhou, Zhejiang Province, China, was placed in laboratory microcosms and incubated in the dark at 25 °C for 182 days to evaluate the feasibility of using the samplers to extract sediment porewater and to estimate NH_4^+ flux across the sediment–water interface under anaerobic conditions. The results show that the samplers were capable of sequentially extracting sediment porewater, 15 ml of which could be readily extracted for analysis within 30–45 min by vacuum applied using a plastic syringe. The NH_4^+ flux under laboratory conditions was characterized by a fast phase during the initial 18 days of incubation followed by a slower linear phase, with average release rates of 11.6 and 3.6 $\text{mg N m}^{-2} \text{d}^{-1}$, respectively.

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1. Introduction

Nitrogen (N) is one of the factors limiting algal growth in eutrophic waters. It is generally recognized that organic-rich sediments can act as important sources of N to the water column of shallow lakes, especially when external inputs are greatly reduced. In the past decade, N cycling has been documented in a variety of aquatic environments, including lake sediments (Carignan and Lean, 1991; D'Angelo and Reddy, 1993; Reddy et al., 1996; Van Luijn et al., 1999), marine and estuarine sediments (Kemp et al., 1990; Sumi and Koike,

1990) and wetlands (D'Angelo and Reddy, 1994a,b; Zhu and Ehrenfeld, 1999).

Studies have shown that NH_4^+ regenerated during microbial decomposition of sediment organic matter can then be transported to the water column via diffusion, sediment resuspension, bioturbation and gas ebullition. The contribution of each path to NH_4^+ flux has varied significantly in different studies. Carignan and Lean (1991) reported that during summer anoxia, 70% of the hypolimnetic accumulation of NH_4^+ was accounted for by diffusion from the sediments of William Bay, Canada. In contrast, the results of Reddy et al. (1996) suggest that dissolved NH_4^+ transport from the surface 8 cm of sediment was due to sediment resuspension, and below this depth upward mobility of NH_4^+ was regulated by diffusion.

Data on NH_4^+ concentrations in porewater are needed to quantify the diffusive flux of NH_4^+ using Fick's

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first law. Generally, porewater sampling methods can be classified as non-destructive or destructive. For instance, porewater can be sampled *in situ* by passive equilibration with the close-interval sampler, first introduced by Hesslein (1976), and its modifications (Shaw and Prepas, 1989). More recently, a practical device that allows simultaneous and sequential sampling of porewater at different depths at the same location was described by Ugo et al. (1999). In addition, porewater can be extracted by means of destructive methods such as pressure filtration, centrifugation and anaerobic centrifugation. The last two methods are commonly adopted in laboratory studies. A review comparing the advantages and disadvantages of various soil solution sampling techniques has been recently published by Song et al. (2000).

The 'Rhizon SMS' soil moisture sampler (Rhizosphere Research Products, Doderstraat 62, 6706 JG Wageningen, The Netherlands) is a small, simple and easy-to-use device capable of sequential extraction of soil solution *in situ* (Wu and Luo, 1999). Due to its simplicity in installation and high temporal and spatial resolution, the suction sampler has been widely used to study chemical processes that occur in soil zones such as the rhizosphere. However, to our knowledge, no attempt has ever been made to extract sediment porewater using this type of sampling device.

The objectives of this study were to evaluate the feasibility of using small soil moisture samplers to extract sediment porewater and to determine the rate of NH_4^+ release from lake sediments during anaerobic incubation.

2. Materials and methods

2.1. Study site and sampling

The samplers were evaluated using sediment samples collected from West Lake, a shallow hypereutrophic lake located in Hangzhou city, East China. The lake has a surface area of 5.66 km² and an average depth of 1.56 m. Factors such as the small storage capacity, insufficient water supply and long hydraulic retention time, and especially the excessive nutrient inputs from human activities in the past few decades have contributed to the hypereutrophic conditions in West Lake. Studies have shown that the surface sediments are characterized by high organic carbon content (average 129 g kg⁻¹, maximum 219.6 g kg⁻¹) and rather high N content (average 1.01 g kg⁻¹, maximum 1.55 g kg⁻¹) (Wu et al., 1990). Bulk sediments were collected on 18 October 1999 from the flocculent layer (0–30 cm) near the centre of West Lake. Subsurface water samples were also collected from the same location.

2.2. Batch incubation experiment

A batch incubation experiment was conducted in quadruplicate using cylindrical polythene containers. A small hole was drilled on the sidewall 0.5 cm above the base of the container, and a soil suction sampler was inserted through a rubber stopper to the centre of the container. Thoroughly homogenized wet sediment (1675 g, equivalent to 201 g dry sediment) was placed into a 3454 ml container and then 1250 ml of filtered West Lake water was carefully added. The containers were sealed with rubber stoppers that held a redox (Pt) electrode, an Ag–AgCl electrode, a compound pH electrode and a thermometer (Fig. 1). The Pt electrode and the compound pH electrode were carefully placed so that their sensors could be inserted about 1 cm into the sediments when the containers were plugged with the rubber stoppers. After the headspace was replaced with 99.999% pure N₂, the container was sealed with silicone glass cement and then incubated in the dark at 25 °C. The pH and Eh of the sediments were monitored regularly, and the Eh measurements were converted to pe values using the Nernst equation. On days 0, 28, 39, 53, 63, 78, 91, 104, 127, 147, 167 and 182, 15 ml of porewater was extracted using a plastic syringe connected to the suction sampler. The airtight containers were then uncovered and 75 ml of overlying water was withdrawn using a large syringe. The 90 ml of water removed was replenished with fresh West Lake water after filtration through ashless filter paper, and the headspace was purged with 99.999% pure N₂. The containers were then sealed and incubated in the dark at 25 °C until the subsequent sampling time.

Overlying water samples were filtered through 0.45 µm pore size membrane filters before analysis for NH_4^+ using Nesslerization. The NH_4^+ concentrations in the porewater samples were determined directly using the same method.

Cumulative NH_4^+ fluxes across the sediment–water interface were calculated from the equation given by Jin and Tu (1990) and diffusive fluxes of NH_4^+ were estimated using Fick's first law. The results are presented as the mean values of four replicate samples.

Fig. 1. Schematic diagram of the experimental setup used in the laboratory study.

3. Results

3.1. The pe and pH dynamics in the sediment

During the first 10 days of incubation, sediment pH decreased from 7.16 on day 0 to 6.87 on day 10. Thereafter, sediment pH was almost stable at around 6.86 ± 0.02 until day 109, when the pH began to decline and finally stabilized at 6.79 ± 0.02 from day 117 (Fig. 2). Sediment pe value dropped sharply from -3.1 on day 0 to -7.6 on day 8. Then it began to rise and reached -6.4 on day 31. The sediment pe subsequently decreased slowly to -7.1 (Fig. 2).

The pe and pH data indicate that the sediment was under nearly neutral and highly reduced conditions throughout laboratory incubation. Under such conditions, NH_4^+ would be the dominant N species and CH_4 production would be expected to occur.

3.2. Porewater sampling

At selected sampling dates, a plastic syringe was connected to the PVC tube of the suction sampler. About 30–45 min were required to extract 15 ml of sediment porewater by vacuum applied using a syringe. As the solution passed through the porous polyester tube of the sampler with average pore size of $0.1 \mu\text{m}$ (Wu and Luo, 1999), the porewater that collected in the syringe was clear and ready for analysis. This avoided the possible exposure of the porewater sample to air with consequent changes in chemical composition. Extraction of porewater with the suction sampler was also less laborious than methods involving filtration and centrifugation. The most important advantages of the suction samplers were their convenience and their capacity to extract sediment porewater in situ, both non-destructively and sequentially.

Fig. 2. Sediment pe and pH dynamics during anaerobic incubation.

Fig. 3. NH_4^+ concentrations in overlying water and porewater during incubation. Bars: standard errors.

3.3. NH_4^+ concentrations in overlying water and porewater

NH_4^+ produced during anaerobic decomposition of sediment organic matter could be (1) adsorbed and fixed by fine particles such as clay minerals and referred to as exchangeable NH_4^+ , (2) released into the porewater to maintain the balance between exchangeable NH_4^+ and NH_4^+ concentration in the porewater, (3) assimilated into organic N by microorganisms, and (4) transported to overlying water by means of diffusion or sediment resuspension. In the absence of nitrification and coupled denitrification, NH_4^+ would accumulate in the water column.

As shown in Fig. 3, the NH_4^+ concentration in the overlying water showed a two-stage pattern. In the initial 18 days of incubation, the NH_4^+ concentration increased from 2.05 mg l^{-1} on day 0 to 7.29 mg l^{-1} on day 18. Correspondingly, the NH_4^+ concentration in the pore water dropped from 10.15 mg l^{-1} to 9.05 mg l^{-1} . Thereafter, the differences between NH_4^+ concentrations in the overlying water and the porewater were much smaller. The overlying water appeared to have reached equilibrium with the porewater with respect to $\text{NH}_4^+\text{-N}$. However, a *t*-test indicated that no significant difference at the $p < 0.05$ level occurred between NH_4^+ concentrations in overlying water and porewater from day 63 to day 104.

4. Discussion

During the initial 18 days of incubation, the increase in overlying water $\text{NH}_4^+\text{-N}$ concentration was accompanied by a decrease in porewater $\text{NH}_4^+\text{-N}$ concentration. The increase in overlying water NH_4^+ concentration may have been due to diffusive flux of NH_4^+ from the sediment. To test this assumption, the diffusive flux of NH_4^+ was calculated from the porewater profiles using Fick's first law:

$$J = -\phi D_s (dC/dx) \quad (1)$$

where J = diffusive flux of NH_4^+ in mass per unit area per unit time; ϕ = porosity (volume of water/unit volume of sediment); D_s = whole-sediment diffusion coefficient in terms of area per unit time; and dC/dx = concentration gradient at sediment–water interface. According to the method of Song (1997), D_s was calculated as follows:

$$D_s = \phi^2 D_0 \quad (2)$$

where D_0 = the ideal diffusion coefficient of NH_4^+ in infinitely diluted solution, and dC/dx can be roughly replaced with $\Delta C/\Delta x$, the concentration difference near the sediment–water interface. As NH_4^+ concentrations in overlying water and porewater were always changing, for simplicity we assumed that the concentrations changed linearly. The value for D_0 was taken from Song (1997) to be 19.8 in units of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The value for ϕ was determined in this study to be 0.88. On the assumption of linearity stated above and the experimental data, the calculated average NH_4^+ flux during the first 18 days was $10.93 \text{ mg N m}^{-2} \text{ d}^{-1}$. This value was very close to the flux value calculated based on the changes in overlying water NH_4^+ concentration ($11.64 \text{ mg N m}^{-2} \text{ d}^{-1}$). The close correspondence of these two methods of calculation confirms that diffusion was the dominant process in the first 18 days of incubation.

Similarly, diffusive fluxes for other periods were calculated. However, significant differences were found between the measured flux and the diffusive flux calculated using Fick's first law (data not shown). In most cases, the calculated fluxes were much smaller than the measured fluxes. The difference between measured and diffusive flux may be caused by (1) NH_4^+ released directly from the sediment–water interface, and (2) NH_4^+ transported to the water column via CH_4 ebullition, which is very likely to occur under strongly reducing conditions.

Based on the overlying water data presented in Fig. 3, the cumulative NH_4^+ flux across the sediment–water interface could be calculated. The trend in cumulative

Fig. 4. Cumulative NH_4^+ flux across the sediment–water interface. Bars: standard errors.

NH_4^+ flux was similar to that observed for overlying water NH_4^+ concentration (Fig. 4). A fast increase in NH_4^+ flux between days 0 and 18 was followed by a steady increase at a slower rate. A linear regression was calculated for the data of the slow phase. The average release rates were $11.64 \text{ mg N m}^{-2} \text{ d}^{-1}$ for the fast phase and $3.6 \text{ mg N m}^{-2} \text{ d}^{-1}$ ($R^2 = 0.9776$) for the subsequent slower phase.

5. Conclusions

This study has demonstrated that 'Rhizon' SMS samplers can be used to extract sediment porewater in laboratory studies. They are convenient devices for use in microcosm experiments and permit repeated sampling with minimal disturbance of the experimental system. In our study, the NH_4^+ release was characterized by a fast phase followed by a linear slower phase. Diffusion was found to be the dominant process in the initial fast phase of NH_4^+ release.

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