

An automated trapping system for improved estimates of N₂O and CO₂ efflux from soil

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Background and Objectives. The production and release of greenhouse gases from soils is a contemporary issue of great social and scientific concern. Many of these gases, particularly carbon dioxide (CO₂) and nitrous oxide (N₂O), are increasing rapidly in the atmosphere, and the processes controlling their dynamics are greatly influenced by human activities such as land management and alteration of the global N cycle (IPCC 2007). The balance between CO₂ uptake during photosynthesis and its release via respiration (i.e. Net Ecosystem Exchange) is an important control on both terrestrial carbon storage and global climate. Although CO₂ fluxes can be well-characterized using micrometeorological and modeling techniques, enhanced spatial and temporal resolution of the factors controlling that balance is essential for resolving the role of the terrestrial biosphere in the global carbon cycle (Valentini et al. 2000). Annual N₂O fluxes, in contrast, are poorly-constrained and exhibit high spatial and temporal variability (Robertson 1993, IPCC 2007). Capturing and understanding this variability is vital if we hope to mitigate N₂O emissions through land management practices and implement successful carbon credit systems.

Tools that improve our ability to quantify N₂O and CO₂ fluxes from soil and constrain annual budgets are therefore needed. Traditional flux chamber (e.g. Ambus and Robertson 2006) and micrometeorological approaches (e.g. Valentini et al. 2000) provide limited resolution and no actual process level information such as sources of respiratory CO₂ or the microbial origins of N₂O. A more mechanistic view of soil fluxes and the microbial processes that control those fluxes is crucial for predicting ecosystem responses to shifts in land management (e.g. new cropping systems) and global environmental change. Here, we propose the development of an Automated Trace Gas-Trapping System (ATGTS) to provide robust estimates of soil CO₂ and N₂O flux and relate that flux to particular microbial metabolisms using novel stable isotopic techniques. Specifically, our objectives are to:

- 1. Develop a novel instrument that provides spatially and temporally meaningful measurements of N₂O and CO₂ flux from soil and, thereby provide significant improvements to estimates and predictions of annual terrestrial fluxes.***
- 2. Design a system that traps sufficient quantities of gas for understanding sources of respiratory CO₂ and the importance of specific microbial pathways of N₂O production based on stable isotope techniques.***
- 3. Design an instrument that is functionally simple (easy to deploy and operate), inexpensive to manufacture, and can be widely used in variety of managed and natural ecosystems by scientists, educators, as well as public and private land managers/owners.***

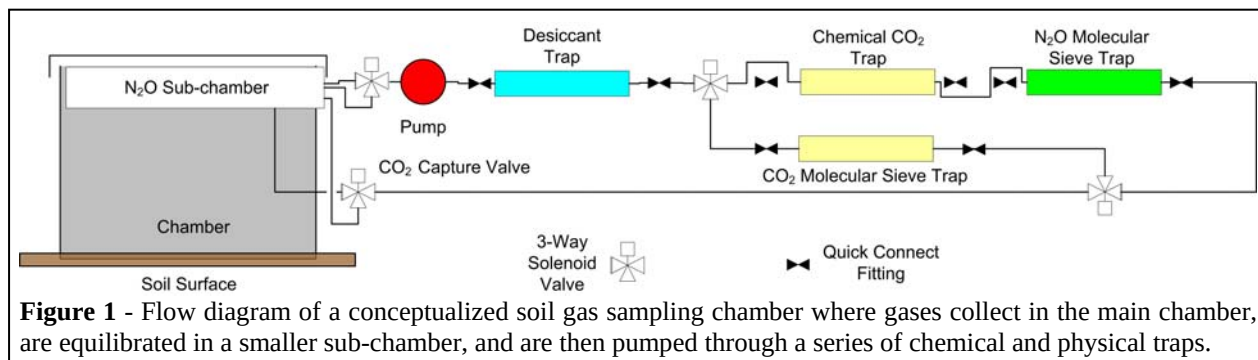
An ATGTS could provide low-cost continuous sampling on a scale of weeks to months and integrated CO₂ and N₂O sample for isotopic and isotopomer analyses of C, N, and O. Our approach is to use gas adsorbing molecular sieve 5Å to trap CO₂ and N₂O continuously over time for later extraction and analysis. Our instrument will use microprocessor-controlled pumps and valves to extract aliquots of atmospheric sample from a chamber at pre-defined intervals, and then move the sample through a series of physical and chemical traps. The result will be separate collections of CO₂ and N₂O integrated over a defined sampling period (e.g. 1 month) that can provide accurate estimates of net flux and sufficient sample for isotopomer measurements, and allow us to capture variability associated with environmental change and event-driven alterations of microbial biogeochemistry.

The ATGTS would be a powerful yet inexpensive and easy to use instrument; however, the development of a working prototype (ultimately leading to a production model) is challenging from a biologist's perspective, necessitating knowledge of micro-processors and electrical circuitry. Such an endeavor would be expedited with the help of an interdisciplinary team possessing the necessary engineering and design knowledge. Thus, we are requesting BERI funds to form an interdisciplinary team of electrical and mechanical engineering undergraduate students to help us develop a working prototype of the ATGTS that can be used for rigorous field testing in spring 2009.

Fundamental approach. The novelty of this proposed sensor is that it uses physical adsorbents to trap and accumulate gas samples for later analysis. Zeolite molecular sieves have uniform pores ranging from 0.3 to 1.0 nm in size and are commonly used to separate or trap gases by selectively adsorbing molecules in that size range or smaller and excluding larger molecules. The molecular dimensions of both N_2O and CO_2 fall perfectly within that range, and molecular sieves have therefore been used to collect and concentrate gases of low concentration. Yoshida and Matsuo (1983) utilized molecular sieve 5Å to accumulate sufficient atmospheric N_2O to estimate $\delta^{15}\text{N}$ in N_2O , and others have used molecular sieve 5Å in passive samplers to develop methods for estimating N_2O emissions from soil (e.g. Duxbury and Voghel 1982, Godbout et al. 2006b). However, Godbout et al. (2006a) measured N_2O desorption recovery of only 88%, which is not sufficient to avoid significant isotopic fractionation. *To our knowledge, an automated molecular sieve trapping system with high recovery of trace gases and no significant isotopic fractionation has not been developed.* We hope the ATGTS will transcend many of the problems associated with previous trace-gas flux measurement systems and improve our understanding of terrestrial net ecosystem exchange and the N cycle.

In order to achieve this and fulfill the stated objectives for this project, the ATGTS will need to provide continuous measurement of N_2O and CO_2 over a period of weeks to months regardless of weather events and allow sufficient flow rate for relatively rapid headspace purging/scrubbing (in order to reduce power requirements), but slow enough to promote complete adsorption of N_2O on the molecular sieve. It needs to be compact and easily deployable, yet with sufficient chamber area to encompass spatial variability; and although solar power is desirable to minimize battery size and power requirements, the system should have sufficient power to operate for one complete cycle (e.g. 1 month) and function in low light environments (i.e. under forest canopy). After CO_2 and N_2O are trapped from the system, the chamber atmosphere should be equilibrated with the atmosphere, as internal chamber temperature and soil moisture should approximate ambient conditions. Gas recovery from molecular sieve after trapping must be close to 100% with no significant isotopic fractionation.

We propose a system where soil gases accumulate in a large chamber, equilibrate with a smaller sub-chamber, and, at regular intervals, gases in the sub-chamber are pumped through a series of chemical and physical traps to remove H_2O , CO_2 and N_2O . The ATGTS would be electronically automated with controlled and timed events. Figure 1 provides a schematic of the necessary components. H_2O and CO_2 compete with N_2O for sites on molecular sieve. Therefore, to estimate N_2O flux, chamber headspace gases would move through a desiccant trap to remove H_2O and then through a chemical trap to scrub CO_2 before N_2O is trapped on molecular sieve. A second event would then repeat the process but bypassing the chemical trap and trapping CO_2 on molecular sieve. N_2O would also be trapped on this second

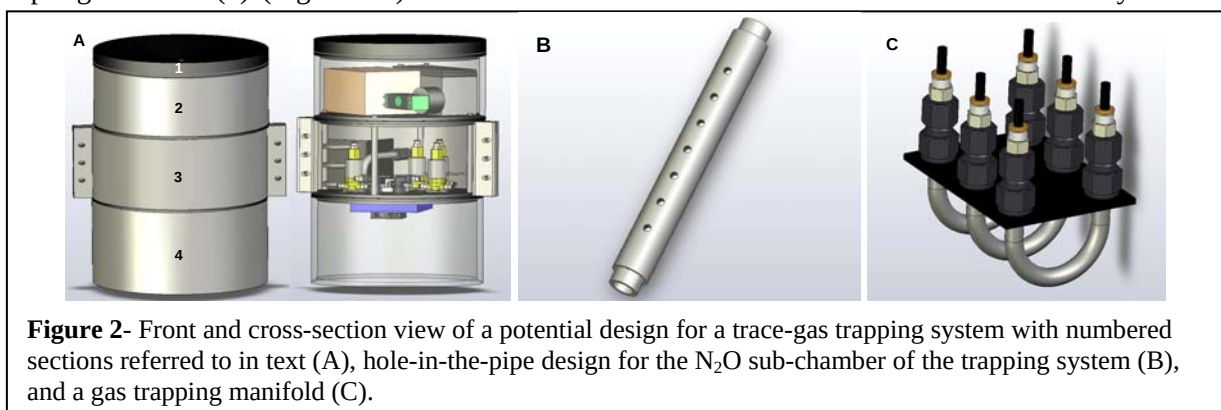


molecular sieve trap, but the concentration of N_2O is many orders of magnitude less than CO_2 and will not significantly influence the adsorption of CO_2 . This process would then repeat itself at intervals for a pre-determined period of time, allowing CO_2 and N_2O to accumulate. At the end of the measurement period, the traps will be removed and gases extracted and measured for concentration and stable isotopes.

In developing the ATGTS several design issues need to be taken into consideration. First are shape, exterior dimensions, and component configuration. The ATGTS must allow for thorough mixing of the headspace gases and not alter the chamber environment. The production and flux of both CO_2 and N_2O are sensitive to soil moisture and temperature, and the ATGTS should maintain surrounding temperatures and rainfall conditions. The ATGTS chamber must also provide sufficient spatial coverage while minimizing chamber volume. Figure 2 shows conceptual CAD drawings of a potential design. For this proposed design, we use a round chamber that can be easily manufactured from commercially available PVC pipe, maximizes soil surface area, and is white and opaque to help maintain ambient internal chamber temperatures while inhibiting CO_2 uptake and transpiration in the chamber.

Another important consideration is the volume of CO_2 , N_2O , and H_2O that needs to be trapped at each trapping interval. It is not practical to trap gas from the entire chamber volume as doing so would likely exceed or hinder the trapping capacity of chemical and molecular sieve traps. Consequently, we propose to subsample the chamber and significantly reduce the amount of chemical scrubbers needed while still providing ample quantities of N_2O and CO_2 for precise flux and isotope measurements. Currently, we are proposing a sub-chamber called the hole-in-the-pipe design (Figure 2B), which consists of two pipes with aligned holes. The internal pipe is plumbed in line with the trapping system, and the external pipe rotates via a servomechanism. The holes of the pipes would be lined-up when the chamber is in rest mode, and a small fan would mix the chamber volume and the headspace of the pipe prior to the trapping cycle. The external pipe would rotate 90 degrees just prior to the pump turning on.

The design concept in figure 2 allows for consolidating the automated portion of the ATGTS into mechanical (3) and electrical sections (2), as well as a rain collection section (1) on top of the main sampling chamber (4) (Figure 2A). Gas flow from the main chamber would be controlled by a small



diaphragm pump in section 3. Gas flow is directed by two and three-way solenoid valves seen in section 3, which would pull gas from the sub-chamber in section 4 and move it through the gas traps. All events would be controlled by a microprocessor controller box in section 4, which is operated by a 12 v battery. All events would be coordinated by a quartz clock, and logged, including system faults, to flash memory on the processor board. After the ATGTS has undergone a complete trapping cycle, a two-way diaphragm pump in section 2 would pump outside air into the chamber through the rain collector on the top of the instrument (section 1). This pump functions for both liquid and air, thus any rainwater present in the collector would be applied to the inside of the chamber via a small nozzle. The other half of the pump would simultaneously pump air from inside the chamber to the outside to purge the excess CO_2 and N_2O , and re-equilibrate the chamber with the atmosphere. System malfunctions could be monitored by using pressure sensors as a fault check for the system. If flow rate increases or decreases beyond a defined

operating range, the ATGTS would immediately shut down, the date, time, and current event status recorded, and a red LED light would blink to let the user know the system has shut down due to a problem. The sample could then be recovered regardless of how long the instrument has been running.

Because build-up of CO₂ and N₂O can cause end-product inhibition of microbial processes and slow diffusional processes, the ATGTS would be programmed to cycle every 4-6 hours depending on expected fluxes within the ecosystem. This should allow sufficient build-up of soil gases, but not to the point of influencing flux rates. At each trapping cycle, the pump will operate for a sufficient period of time to move 2-3 volumes through the sub-chamber. At a pumping rate of 300 mL/min and a sub-chamber volume of 150 mL, the pump would need to circulate for 1-1.5 min. The chamber purging and rainwater collection pump operates at closer to 1.5 L/min, and would therefore operate for 4-6 minutes for a 3 L chamber. Thus, each cycle would take less than 10 min every 4-6 hours. We will then correct for the soil CO₂ and N₂O flux that occurs during that period of time based on the average flux calculated at the end of the measurement period (e.g. 1 month).

Power is a potential pitfall of which we need to be cognizant. We intend to run the ATGTS on a 6 or 12 v battery with back-up solar charging for extended run times and only exchange chemical traps as necessary for continuous measurement. However, we do not want to exclusively depend on solar power as this would limit applications of the instrument. Battery swapping is another option, or having an auxiliary power plug on the side for adding additional batteries or using AC power when logistically possible. The best solution for addressing the power issue is to have the instrument be as efficient as possible with minimum run time and power consumption. Table 2 provides a calculated power budget

Table 2- Power budget for the proposed ATGTS using commercially available components and circuit boards.

Device	# required	Voltage (Volts)	Power (Watts)	Current (Amps)	Time each cycle (s)	Time each cycle (hrs)	Run hours (1 month)	Amp*Hours (4 Hours)	Amp*Hours (Month)	Total Amp hours per month
3-Way Solenoid Valve	4	12	3	0.2500	2	0.001	0.1	0.0001	0.025	0.1
KNF .25 -.45 l/min Micropump	1	6	-	0.0001	120	0.033	6	0.0000	0.0003	0.0003
KNF Dual Head LiquidMicropump	1	12	10.5	0.8750	360	0.100	18	0.0875	15.75	15.75
Circulating Fan	1	12	-	0.1800	360	0.100	18	0.0180	3.24	3.24
Brainstem Controller	2	12	-	0.0250	14400	4.000	720	0.1000	18	36
Linear Solenoid	1	12	3	0.2500	8	0.002	0.4	0.0006	0.1	0.1
Total amp hours needed for a 1 month cycle										55.1903

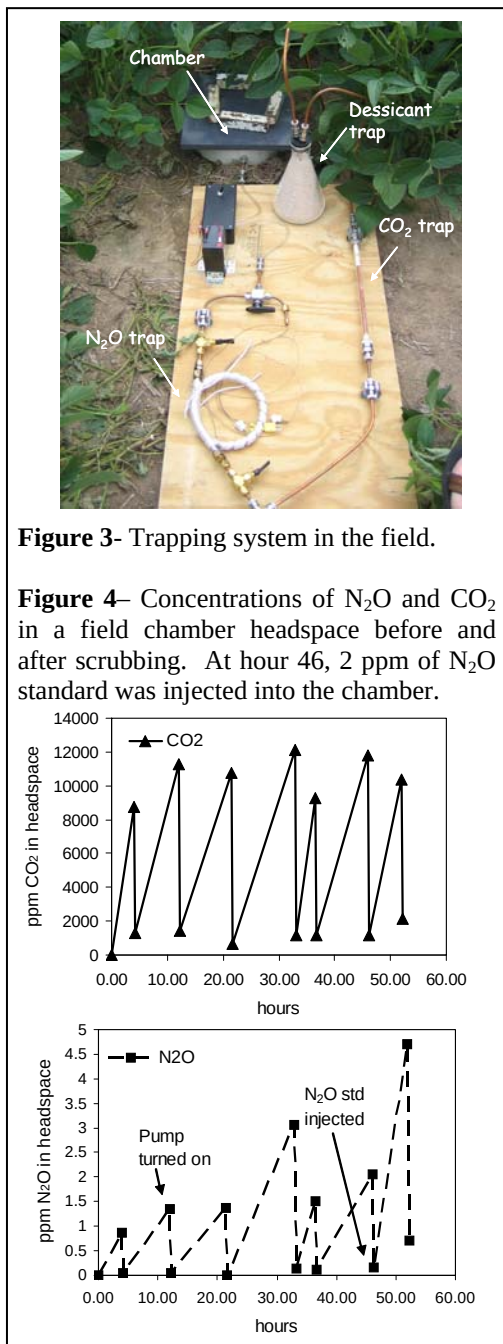
based on the component requirements for the proposed system. The total DC power requirements for one month are 55 amp hours. Most small 6-12 volt commercial rechargeable batteries supply roughly 5 amp/hours of power, suggesting we need a much larger battery source or multiple batteries. However, much of that power draw is from the constant power supply to two circuit control boards and the dual head pump for venting the chamber. We feel this can be substantially reduced by using alternative pumps and circuit boards, and turning off power to the control boards between cycles. Overall, we expect that the engineering team could help us reduce the power budget and develop a small lightweight sensor.

Proof of concept. To test the ability of molecular sieve 5Å to adsorb and release N₂O and CO₂ with high rates of recovery and no isotopic fractionation, we performed a series of preliminary experiments using standard tank N₂O with known δ¹⁸O and δ¹⁵N values and a sealed chamber made out of large diameter PVC pipe. CO₂, N₂O and H₂O traps were attached to the chamber with stainless steel (SS) tubing and the system circulated with a SS bellows pump. Once the chamber was completely purged with N₂, pure N₂O and CO₂ were injected into the chamber, and the chamber circulated for 5 minutes. Headspace gas samples were analyzed for N₂O and CO₂ concentrations. Traps were then added sequentially at 5 minutes (CO₂ trap) and 15 minutes (N₂O trap). After 25 minutes, the CO₂ trap was removed and pure CO₂ was injected into the system to test the stability of N₂O on the molecular sieve. This experiment was conducted on three different dates with similar results. We found that N₂O and CO₂ were readily adsorbed. Moreover, CO₂ pulses did not facilitate the release of N₂O from molecular sieve. At the end of

each experiment, N_2O was desorbed from the molecular sieve traps to examine the uptake efficiency, stability and recovery of N_2O . N_2O was removed from the molecular sieve upon heating and collected under vacuum in a cryogenic trap and then analyzed for isotopomer abundances. Our results demonstrated that N_2O is conserved on molecular sieve for relatively long periods (weeks) and can be removed at high temperature with near 100% recovery and no measurable isotopic fractionation. We have not conducted these trials with CO_2 , although isotopic integrity of CO_2 on molecular sieve has been demonstrated previously (Godbout et al., 2006a, b).

To further demonstrate the feasibility of the ATGTS, we adapted the previous system for field trials. The bellows pump was replaced with a 6 volt DC KNF-Neuberger mini-diaphragm pump with a pump rate of ~ 500 mL/min. Trials were conducted at the KBS-LTER site using the chamber configuration in Figure 1 (see Figure 3). Every 4 hours, a gas sample from the chamber headspace (3.5 L) was collected through a septum in the side of the chamber. The chamber headspace was then circulated internally through the gas traps for 10 minutes, another gas sample taken from the headspace, and then cycled to the atmosphere for 10 minutes. Before and after samples were then analyzed for CO_2 and N_2O concentration. This experiment was completed 3 times for periods ranging from 52-76 hours. We found that at each trapping event, the N_2O in the chamber headspace was reduced to 0 (Figure 4). The CO_2 concentration did not always reach zero due to the high CO_2 flux rate relative to the chamber flow rate, but was very low. Results of these trials demonstrate that this system can effectively remove N_2O and CO_2 and provide accurate flux estimates over long time periods.

Budget. We request funds according to the BERI proposal guidelines. We would allocate \$5-6k the \$10k award towards the support of the engineering team, with the remainder going toward supplies. Any further needed supplies will be supplemented by the Smemo and/or Roberston Labs. Overall, we feel this project will benefit from the continuity and shared intellectual ownership among the complement of investigators and the engineering team. Together we would have the expertise, experience, and equipment needed to successfully develop this important instrument, while at the same time offering MSU engineering students a uniquely collaborative and rewarding Senior Capstone Design experience.



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