

**New Ozone Measurement Systems for Autonomous Operation
on Ocean Buoys and Towers**

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Abstract

We have built and tested two autonomous ozone measurement systems for use on ocean buoys and towers. They are based on low-power atmospheric ozone sensors from Physical Sciences Inc. (PSI) and 2B Technologies. The PSI sensor operates at 1 Hz with a precision of 1 ppb, but requires about 45 W with the present data system; the 2B makes a measurement every 10 seconds with a precision of 1-2 ppb and uses less than 4 W. The sensors have been packaged in watertight enclosures, with a set of valves and filters to keep out seawater and aerosols. A controller uses data from the sensors and a meteorological system to determine whether sampling should proceed. If a sensor malfunction (such as an incorrect valve position or a temperature beyond its proper range) is detected, the controller attempts to correct it. Both sensors have been tested and used over the ocean, and one complete ozone measurement system (with the PSI sensor) has been successfully deployed on a buoy off Woods Hole. In 2003, this system was operated at the Chesapeake Bay Lighthouse Tower for over a month with excellent results. The 2B system was also successfully tested in 2003, at a nearby offshore tower. The design of the systems and their testing and deployments are described, and data from some of the first experiments are presented.

Introduction

Tropospheric ozone plays a variety of roles in atmospheric chemistry. It is an oxidant as well as the principal source of the OH radical, which acts as a “cleanser” of the atmosphere. Even at relatively low levels (60-80 ppb), ozone causes respiratory problems in humans, and crop damage can occur at even lower levels (e.g., Mauzerall and Wang, 2001; Brunekreef and Holgate, 2002). Though it is an important greenhouse gas, it also acts to prevent the buildup of other greenhouse gases (hydrocarbons in particular) through its role in HO_x (OH and HO₂) chemistry and oxidation. This oxidation chemistry is particularly important over the tropical and subtropical oceans (Crutzen et al., 1999), but is also significant at higher latitudes.

Current areas of interest involving tropospheric ozone include pollution monitoring, the “oxidative capacity” of the atmosphere, ozone trends over time, the influence of stratospheric ozone on the troposphere, and the coupled chemistry and transport patterns that lead to present ozone levels throughout the world. Because of its importance, there are large networks of land-based ground sites in place throughout the world where ozone and other chemical and meteorological parameters are measured, as well as sonde stations for ozone profiling. Yet these stations come to an abrupt end at coastlines, leaving about 70% of earth’s surface without observations. Another topic that has recently gained attention is the long-range transport (both regional and intercontinental) of anthropogenic emissions, including ozone and ozone precursors (e.g., National Academy of Sciences, 2001). Intercontinental transport occurs almost by definition across oceans, with the principal pathways being export from North America to Europe over the Atlantic Ocean (e.g., Stohl and Trickl, 1999, Li et al., 2002) and transport from Asia to North America across the Pacific (Jaffe et al., 1999). To address this, air and ground-

based studies have been conducted over both ocean basins (e.g., Fehsenfeld et al., 1996; Hoell et al., 1996), as well as over the Indian Ocean (Ramanathan et al., 2001).

However, measurements over the oceans and in other remote locations have been very sparse, particularly compared to populated continental areas. Satellite observations provide global coverage, but measurements in the troposphere are still in the early stages (e.g., Newchurch et al., 2001; Ziemke et al, 2001) and are generally not possible near the surface of the ocean. An improved understanding of atmospheric chemistry and transport will come only with the ability to measure key species throughout the world, at times and locations as desired. We have therefore begun a project to develop atmospheric instrumentation for deployment on ocean buoys and other remote platforms almost anywhere over the oceans. This paper describes our first instruments and measurement systems for tropospheric ozone.

Instrumentation

The objective of this work is to develop and deploy high-quality sensor systems, in order to investigate chemistry and transport in the marine boundary layer and air-sea interactions. The remote marine atmosphere presents two particular problems: the harsh environment and the limited availability of electrical power. Moreover, our systems need to be able to operate for months at a time without direct human intervention. For use in the marine environment, we have packaged the components in watertight containers, chosen compatible materials for all external pieces, and designed a system of valves to protect the instruments during potentially hazardous conditions (high winds, rain, and sea spray). The systems are controlled by an external computer (controller) that checks whether key components are operating properly and can reset the instrument or shut it down if necessary. The range of acceptable conditions can be set on the

controller, which monitors meteorological data from a small subsystem. Power can be provided by batteries, with or without solar panels, or from a generator. For operation on buoys, however, the power limitation is a severe one, and has forced us to choose our targets carefully. Because ozone is such a central and important species in the marine atmosphere and it can be measured with low-power sensors, it became our first objective. In the following sections, the individual components of our systems and their performance are described.

Ozone sensors

Our two ozone sensors were obtained from Physical Sciences Inc. (PSI), Andover, MA, and from 2B Technologies, Golden, CO (www.twobtech.com). These have both been packaged for use on buoys and towers, and tested and operated in the marine environment over the last two years. Basic characteristics of the two sensors are listed in Table 1.

I. PSI photometer

The PSI ozone photometer is patterned after a compact, low-power, high-altitude instrument developed by Rawlins, Proffitt, and coworkers (Rawlins et al., 1997; Ross et al., 2000). The basic design derives from larger flight instruments of Proffitt and coworkers, with ozone measurement accuracy and sensitivity comparable to that of the NOAA ER-2 photometer (Proffitt and McLaughlin, 1983), but with improved thermal stability, lower power consumption, and smaller flow rate requirements. It typically uses 45-60 W at 24-27 VDC during normal operation, and has a photometric noise-limited detection sensitivity of 3×10^{10} molecules/cm³ at 1 Hz, or 1 ppb at sea level, compared to 0.5 ppb for the NOAA photometer (which has an absorption path length twice as long).

A temperature-controlled aluminum block is used to make a dual-beam absorption cell

with two matched optical paths 20 cm in length. Three Teflon-coated 0.25-inch dia. channels serve as the optical and flow paths, as shown in Figure 1. Air passes through Teflon tubing into the central channel of the block, where it is pre-heated and split into catalytically scrubbed (reference) and unscrubbed (sample) flows. Ozone is removed from the scrubbed flow by an array of MnO₂-coated screens. A four-way rotatable valve, made of glass-filled Teflon and driven by a software-controlled stepper motor (Intelligent Motion Systems), admits the separate scrubbed (ozone-free) and unscrubbed (ozone-laden) air flows into the two legs of the absorption cell. Switching of the valve position every 10 seconds interchanges the sample and reference flows. The flow is driven by a small ASF Thomas rotary vane pump on the exhaust and has been adjusted to be fast enough for complete exchange of the air in the cell in about 1 s, but slow enough to avoid dynamically-induced noise in the optical absorbance measurements.

A mirror/beamsplitter assembly directs 254 nm radiation from a mercury lamp (BHK Inc.) along the length of each optical path onto a pair of bandpass-filtered photodiodes (EG&G). The signal current from each photodiode is processed by a low-noise amplifier connected to a high-precision voltage-to-frequency (V/F) conversion circuit as illustrated in Figure 2. To maximize shielding and thermal stability, the amplifier and V/F conversion circuitry are mounted on printed circuit boards embedded in the base of the aluminum block (Figure 1). The frequency output of the V/F converters is sampled at 1 Hz by a counter-timer board with 24-bit resolution and stored on a computer.

The cell block and airflow temperatures are controlled at 33EC by thin film heaters mounted along the sides of the block, in order to maintain it above ambient temperature under most conditions. Gas flow temperatures at the absorption path inlets and outlets, as well as other

system hardware temperatures, are monitored by high-precision thermistors. The airflow pressure at the midpoint of each cell is measured by a pressure-sensing chip (EG&G). The outputs of the temperature sensors, pressure sensors, and other monitors (current and voltage) are connected to an A/D converter with 12-bit resolution. The digital signals are then passed to the instrument computer. The data system, consisting of the computer (Ampro), counter-timer board, and A/D boards, is assembled in PC104 format to minimize size and weight. The control/acquisition software resides on a 16 MB disk-on-a-chip in a DOS environment and the processed data are written to a hard drive.

The nominal 27 V supply voltage is regulated to +5 V, +12 V, and ∇ 15 V by DC-DC converters (Wall Industries). All instrument subsystems use the regulated, down-converted voltages except the valve stepper motor driver and the absorption cell heaters. In particular, the UV light source power supply operates at 12 V, so a drop-off in the platform-supplied voltage below 27 V does not affect the photometer performance.

Data are analyzed to determine ozone mixing ratios using procedures similar to those described by Proffitt and McLaughlin (1983). Briefly, the ratio of the transmitted intensities for the two optical channels gives a square wave whose amplitude is related to the absorbance, $\ln(I_0/I)$. This amplitude is determined every 10 s when the flows are interchanged between the two legs. A linear segment fitting procedure is then used to interpolate from the 10-s determinations to 1-s determinations based on the measured signal ratios. The measured absorbances are converted to ozone number densities by dividing by the 254 nm absorption cross section and the optical path length, and then to mixing ratios with the measured cell pressures and gas temperatures. The instrument was delivered to Woods Hole Oceanographic Institution

(WHOI) in May 2001 and was packaged, tested, and used at sea as described below.

II. 2B Ozone Monitor

The Model 202 Ozone Monitor from 2B Technologies is based on improvements to the design of Bognar and Birks (1996). It was originally built for deployment on tethered kites and is therefore very light (2.1 kg) with low power consumption (3.6 W). A schematic of the instrument is shown in Figure 3.

It uses a mercury lamp for direct absorption measurement of ozone through a 15-cm long quartz absorption cell. Radiation is monitored by a photodiode (Hamamatsu) with a built-in bandpass interference filter at 254 nm, and the signal is converted to a voltage and read by an A/D converter. Air is pulled through the instrument at approximately 1 l/min by a small pump, with the flow alternately passed directly through the cell for measurement of ozone or first through a catalytic scrubber for measurement of the radiation in the absence of ozone, I_o . A solenoid periodically switches the flow with a sequence of 4 seconds of unscrubbed flow and 6 seconds of scrubbed flow. Ozone is calculated every 10 seconds from Beer's Law:

$$[O_3] = \frac{1}{\sigma l} \ln\left(\frac{I_o}{I}\right) \quad (1)$$

where $[O_3]$ is the concentration of ozone, Φ is the absorption cross-section of ozone at 254 nm ($1.15 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, with an accuracy of 2%), l is the (15 cm) path length, and I is the signal in the presence of ozone. Temperature and pressure are measured in the cell in order to calculate ozone mixing ratios. The detection limit is 1.5 ppb, and the stated precision and accuracy are the higher of 2% or 1.5 ppb.

A microprocessor performs all the calculations and can store a few days of data on a small solid-state memory device. Data can also be averaged for 1 minute, 10 minutes, or 1 hour prior to storage. To collect data over long deployments, we transmit 1-minute averaged data over a serial line for storage on flash memory in an external controller as described below. In principle, direct absorption measurement is an absolute method. However, to correct for any nonlinearities in the electronics or other deviations, a small (few percent) correction is applied to the offset and slope by comparing the instrument with a conventional ozone spectrophotometer in the laboratory. In addition, a periodic zero check using an external scrubber is recommended, and has been implemented in our field measurement system.

The ozone measurement system for field use

In order to allow high-quality measurements, long-term unattended operation in remote locations, and protection of all components from the marine environment, we have built watertight enclosures for the ozone sensors and other components, a power supply and controller to run the instruments, and an inlet/outlet system to bring ambient air to the sensors. A schematic of the current ozone system is shown in Figure 4.

The PSI ozone sensor was packaged for buoy deployment in a 55 x 34 x 22 cm anodized Aluminum box and weighs 19 kg, more than half of which is from the enclosure itself. The 2B instrument was packaged in a plastic Rose enclosure, along with its controller and external ozone scrubber for checks of instrument zero. Power can be provided by alkaline batteries or solar panels and rechargeable batteries for buoy operation, or by a battery and charger or DC power supply on platforms with a local source of electricity. All connectors and cables (Subconn and Impulse) are wet mateable and designed for long-duration use at sea.

The controller (based on a Dallas Semiconductor DS87C530 chip) is an ultra-low power (50 mW) single-board computer, which switches power to the ozone sensor through a relay, receives and records data from the ozone sensors and the meteorological instrument package, opens and closes the inlet and outlet valves, and performs a periodic zero check with an external scrubber. It is programmed in C, with adjustable parameters on an EEPROM to set the criteria for shutting down due to wind or rain, and to set the timing and conditions of the zero check. It can also check for sensor malfunctions; for example if the valve position on the PSI instrument deviates from its correct value or the CPU temperature is too high, the instrument is shut down and restarted after a suitable waiting period. This resets the valve position and allows the CPU to cool down. Serial data are sent from the sensor to the controller and stored in flash memory. A console port on the controller can be used to view operating status and send data to or commands from an external computer, or through a network connection, an RF modem (during near-shore operation), or a satellite link.

The present meteorological package consists of a cup anemometer (R. M. Young) and a rain detector (designed at WHOI) based on electrical conductivity between a plate and a grid. Data are sampled by the controller once per minute, and if rain or sea spray are detected or the wind speed exceeds a certain level (typically 10-15 m/s), the controller can be programmed to shut the sensor off and close the inlet and outlet valves to protect the sensor until conditions improve and rain or high winds are no longer detected. The inlet and outlet consist of Teflon ball valves (Teqcom Industries) that are opened and closed by a DC motor with limit switches. These were based on a design that has been successfully used in aerosol sampling instruments of Sholkovitz and coworkers (1998). The external zero check is performed by shutting the inlet

valve and opening a solenoid to route incoming air through an external ozone scrubber before arriving at the sensors. This is typically done once per day. The external scrubber is mounted in a separate housing for the PSI system, and in the same box as the 2B sensor.

Tests and Field Deployments

In fall 2001, the PSI ozone sensor was integrated onto a 3 m dia. discus buoy (Figure 5), along with aerosol and iron/rainwater sensors (Sholkovitz et al., 2001). A central computer recorded meteorological data (wind speed and direction, temperature, relative humidity, and rain), and sent it to the ozone controller. Data could be sent to and from a shore station with an RF line-of-sight modem. Electrical power at 12 V was provided by battery packs of alkaline “D” cells. Other components of the system included a DC regulator to convert 12 V to 27 V, inlet and outlet closure valves, and a simple air inlet (Figure 5). The air intake consisted of a ½" Swagelok PFA Tee, with short sections of Teflon tubing facing forward and backward, and air to the ozone instrument traveling up through the branch of the Tee. A vane attached to the buoy kept the forward-facing tube directed into the wind, such that large (>5 :m) aerosols would pass through the horizontal sections of tubing and not be pumped into the ozone instrument. No filters were used in this deployment.

The buoy was operated in Vineyard Sound, in Woods Hole Harbor, and on land from October 22 to early December. All components of the ozone system functioned, but one of the two channels to measure ozone developed a high noise level (since diagnosed as a mechanical problem and fixed). Data from the low-noise channel during the buoy test are shown in Figure 6. Ozone values were similar to 1-hour averages obtained from the Massachusetts Department of Environmental Protection (DEP) station in Truro, about 75 km NE in Cape Cod National

Seashore, but the buoy data showed more structure on times shorter than 1 hour (e.g., hour 22 in Figure 6a). Over a time scale of minutes, sharp decreases in ozone were also observed (Figure 6b). They are not caused by noise in the system, and are likely from exhaust from passing ships, which removes ozone through the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$. These 1-5 minute decreases (never increases) have also been observed on subsequent deployments in the marine boundary layer.

During the buoy deployment there were no water leaks in any of the components, and the inlet, outlet, other electrical and mechanical subsystems, and software functioned properly. Within the instrument, the lamp, 4-port valve, heaters, pump, computer, and electronics all performed as designed. The only major problems were the increased noise on one data channel, and as expected, the rate of power usage (typically 2 to 2.5 A at 27 V), part of which was caused by the cell heaters switching on more frequently in colder weather. Following the test we began planning several changes to the system to improve this.

In September-October 2002, both the PSI and 2B sensors participated in the AIRS BBAERI Ocean Validation Experiment (ABOVE) on the Chesapeake Bay Lighthouse Tower (36.91 N, 75.71 W), about 20 km offshore from Virginia Beach, VA (McMillan et al., 2002; Fetzer et al., 2003). The AIRS (Atmospheric InfraRed Sounder) instrument is a nadir-viewing grating spectrometer on the NASA Aqua satellite. The BBAERI (Baltimore Bore Atmospheric Emitted Radiance Interferometer) is an interferometer capable of viewing upward or downward, which was deployed on the tower by the University of Maryland Baltimore County (McMillan et al., 2001). The goal was to validate measurements of temperature, humidity, ozone and other trace gases from AIRS in the troposphere. The tower has a diesel generator on board, but the finite supply of electricity and the cost of long-term deployments

suggested the use of a low-power autonomous ozone sensor.

At the time of the first ABOVE experiment, neither ozone sensor had been fully packaged, so both were operated inside a room near the top of the tower, with inlet tubing running up to a small mast about 45 m above the water surface. Both instruments functioned for most of the deployment, but high temperatures in the room (>35EC), lack of ventilation, and direct sunlight on their enclosures caused agreement between the two sensors to drift (PSI 10-20 ppb higher in the day; agreement within 2 ppb at night). In addition, both instruments were left operating during the passage of Hurricane Gustav (which forced the evacuation of the tower), and the PSI instrument became so hot that the CPU occasionally stopped working (>74EC) and the 4-way valve seized twice. Even with these problems, 28 days of useful data were obtained over the 34-day deployment. Clearly, however, the instruments needed to be completely packaged for deployment outside (with adequate ventilation and cooling), shielded from direct sunlight, and protected from rain or severe weather. This was done following the first ABOVE deployment, and both instruments are now packaged as described above.

In June 2003, the fully-packaged PSI system was brought back to the Chesapeake Bay tower for a continuation of the ABOVE experiment. This time it was operated on the service deck of the platform, out of direct sunlight and away from the diesel generator exhaust (which generally flows up and away from the platform). The instrument was run successfully without the controller for one week, and then with the controller, closure valves, and automatic zero-check subsystem. A 2-um Teflon filter (Pall) was placed in line with the flow near the inlet to prevent small aerosols from entering the ozone sensor and tubing. Prior to this deployment, the PSI instrument was certified at the U.S. Environmental Protection Association (EPA) station in

Chelmsford, MA, by comparing with a National Institute of Science and Technology (NIST) standard ozone photometer and verifying that the deviation was always less than 3%. A stock TEI 49C ozone photometer (University of Maryland Baltimore County) was also deployed at the tower, and was operated inside the main building with the inlet suspended below to the service deck, near the inlet of the PSI system. In addition, electrochemical ozone sondes were launched periodically during the first three weeks of the deployment by the University of Alabama at Huntsville.

The autonomous PSI ozone system produced high quality data for the entire 2003 ABOVE deployment, from June 1 to July 7. There were no instrument failures, and because the instrument was positioned under the main deck, nor were there any shutdowns caused by rain. Only the zero checks did not work properly - with the flow passing through the external scrubber, ozone only dropped to about 50% of its ambient value (10 to 70 ppb), almost certainly because of a leak. In previous tests with the PSI instrument, measured ozone was within a few ppb of zero during zero checks with the external scrubber. In addition, for most of this deployment there was no detectable zero offset between the PSI and TEI instruments. Data from the second ABOVE deployment are discussed in the following section.

The 2B system was deployed on the Air-Sea Interaction Tower (ASIT) at the Martha's Vineyard Coastal Observatory (<http://mvcodata.whoi.edu/cgi-bin/mvco/mvco.cgi>), about 3 km south of Edgartown, MA. It successfully operated on the tower from October through early November 2003, and the results are described below.

Results

From buoy tests to the most recent Chesapeake Bay and ASIT tower deployments, the

ozone measurement systems have successfully made measurements for up to a month at a time or longer with minimal intervention. The June-July 2003 Chesapeake Bay deployment provided a particularly good test of instrument performance due to the long duration and the other coincident ozone measurements. A time series of ozone mixing ratios is shown in Figure 7, with data from the PSI and TEI instruments, and ground level data from a series of ozone sondes launched from the flight deck of the tower (about 5 m above the inlets for the PSI and TEI instruments). Both the PSI and TEI instruments tracked well during the majority of this period, with the PSI 6% higher than the TEI (with no offset) for most of the deployment, but in good general agreement with the sondes. For almost a week (Day 157-163) however, the TEI was substantially lower than the PSI and sondes, after which it seemed to recover. No explanation is currently available for this; the discrepancy does not correlate with any meteorological data (wind speed or direction, temperature, humidity, etc.) available at the tower. Figure 8 shows TEI data from Day 163-189 and all the sonde data plotted against PSI data. The PSI was about 3 ppb lower than the sondes, consistent with the general upward trend of ozone with altitude as measured by the sondes and possibly also reflecting some ozone loss on the bare metal of the service deck. It is not clear why the TEI instrument measured lower than the PSI, but this may have been due to ozone loss from contamination of inlet lines, or the instrument calibration. The PSI instrument in principle does not need calibration, but calibration checks have been very useful for demonstrating the presence (or absence) of ozone loss in the inlet.

A time series of ozone from the 2B system at the ASIT tower during the first part of October is shown in Figure 9 (top), along with simultaneous data from the Wampanoag Tribe Laboratory in Gay Head (Aquinnah), MA, about 20 km to the west on Martha's Vineyard. The

two data sets show many of the same features, but there are distinct differences between the land and ocean sites caused by local sources and sinks of ozone and different transport patterns. Average diurnal cycles of ozone are shown in the bottom of Figure 9, and indicate that ozone levels were slightly higher on land during October 2003. During this deployment, the zero check system (and all other components) worked properly on the 2B system and the recorded zero offset was always within $\sqrt{2}$ ppb, with an average less than 1 ppb. The results of the Chesapeake Bay and ASIT tower deployments, including a comparison with nearby land stations, an analysis of the differences between land and ocean stations, and calculations of ozone production and loss over the ocean, will be described in a forthcoming paper.

Conclusions and Future Directions

We have demonstrated that long-duration ozone measurements can be made at sea with reasonably simple low-power systems. These systems are now ready for use in a wide variety of experiments to study ozone chemistry and transport over the ocean, the oxidative capacity of the marine atmosphere, and atmospheric pollution. In the meantime, we are continuing our efforts to improve the reliability of the ozone sampling systems and the performance of the sensors, and to reduce the rate of power consumption.

In 2004, we anticipate that one or both ozone systems will be deployed on a buoy as part of the Northeast-North Atlantic experiment (NENA) in the Gulf of Maine, which follows the New England Air Quality Study and the North Atlantic Regional Experiment (NARE) (Fehsenfeld et al., 1996). In the future, we intend to deploy these systems far from shore, to study ozone chemistry in the remote ocean and intercontinental transport of pollution. In an upcoming study of ozone deposition flux to the ocean surface, one of the ozone systems will

serve to calibrate the signal from a fast ozone sensor for eddy correlation flux measurements to the coastal ocean. We are also developing a low-power CO instrument (from FIS Inc., Japan; Ohta et al., 1999) for use on buoys. The combination of CO and ozone will provide a powerful tool to investigate chemistry and transport over the coastal and remote oceans. Ultimately we envision several small systems (with a 2B ozone sensor and meteorological data) for deployment on existing moorings, and one or two larger packages with both ozone and CO.

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Figure Captions

Figure 1. The PSI absorption cell design with side view (above) and top view (below). Ambient air enters at the sample inlet, is split into two flows, one scrubbed of ozone and the other unscrubbed, and sent separately to the two absorption cells, then recombined in the exhaust. 254 nm radiation from the mercury lamp is split into two beams and directed through the absorption cells before being detected by the photodiodes. The scrubbed and unscrubbed flows are switched every 10 seconds by the 4-port valve.

Figure 2. Electrical schematic of the PSI ozone instrument. Ozone is measured in the absorption cell (Figure 1). Photodiode (PD) signals from the sample and reference cells are converted to frequencies in the transimpedance amplifier (TIA) and voltage-to-frequency (VFC) circuitry, read by the counters, and sent to the computer. See text for details.

Figure 3. Schematic of the 2B ozone sensor. Scrubbed or ambient air is alternately sent through the absorption cell by the solenoid valve, then out through the air pump. Radiation from the lamp is monitored by the photodiode and signal-processing electronics for measurements of I_0 and I .

Figure 4. Diagram of the PSI ozone system, showing the controller, possible power sources, ozone sensor, meteorological instruments, inlet and outlet closure valves, and zero-check subsystem. The 2B system is similar, except that it uses 12 V and the ozone sensor and external ozone scrubber are all mounted in the same box as the controller.

Figure 5. The discus buoy moored in Vineyard Sound in October 2001. The PSI ozone sensor is visible on the left along with the Teflon inlet tube. The controller for ozone is mounted on the right. Parts of the aerosol and rainwater sensors are also visible, as well as the meteorological

instruments. All the instruments were powered by batteries contained in a well in the center of the buoy.

Figure 6. a) 1 Hz (open circles) and 12-minute averaged ozone data (squares) from channel A of the PSI ozone sensor during the buoy test. One-hour average data (filled circles) from the Mass. DEP Truro site, about 75 km to the NE, are also shown for comparison. b) A small subset of the data (1 Hz and 12-minute average), showing variations observed in ozone over time scales of a few minutes. These have a small effect on the 12-minute data but are almost negligible in one-hour averages.

Figure 7. Time series of PSI (squares), TEI (circles), and surface-level sonde data (triangles) from the ABOVE deployment, 1 June - 7 July 2003. Sondes were launched to coincide with AIRS overpasses during good meteorological conditions over the first three weeks of the experiment.

Figure 8. TEI data plotted vs. PSI data for the period when both instruments were operating properly (circles), and sonde data plotted vs. PSI data for all coincident points (triangles). A least-squares fit line of the TEI and PSI data is also shown. The PSI data were approximately 3 ppb lower than the sonde data, with a slope close to unity.

Figure 9. (top) Time series of ozone as measured by the 2B system at the offshore ASIT tower (circles) together with ozone measurements at a nearby shore site (squares) for part of October 2003. (bottom) Average diurnal cycle at the two sites for the period shown above.

Tables

Sensor	PSI	2B
Data rate	1 Hz	0.1 Hz
Precision	1 ppb	2% or 1.5 ppb
Accuracy	2%	2% or 1.5 ppb
Power required	45 W w/heaters off	3.6 W

Table 1. Performance characteristics of the ozone sensors used. The limit of detection of each sensor is approximately equal to the precision. More than half of the power used in the PSI sensor is for the data system.