

Use of Laser Technology to Monitor Ammonia Emissions from Dairy Lagoons

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Abstract:

Ammonia emissions from dairies may be a significant contributor to the San Joaquin Valley, CA, air problem. Our research is currently aimed at identifying and managing these emissions. On a dairy, a source of emissions comes from the dairy effluent filled lagoons. Firstly, we review the technology involved in the use of filter packs and open path tunable diode laser (OPTDL) for monitoring ammonia emissions. Then we present some of our research data collected to highlight the applicability of the OPTDL for monitoring diurnal and seasonal fluctuations of ammonia during various dairy management practices. For example, in a management system comprising of acidification of the dairy effluent acidification coupled with aeration and freshwater addition, we detected ammonia fluctuations as the pH and oxidation reduction potential levels of the lagoon water changed. In summary, we found that as the pH of the lagoon dropped from 8.0 to 6.5, average NH₃ fluxes decreased from approximately 1.6 to 0.5 mg/m²/s. Generally, relatively high gas fluxes were detected at the start of the aeration, probably due to agitation of the lagoon, followed by a gradual reduction as the lagoon was subjected to further aeration, acidification, and fresh water addition. Due to the limited number of laser units available we are currently unable to obtain simultaneous upwind and downwind concentrations. Hence, a major draw back of using the data collected with the OPTDL in an EPA approved model to predict downwind concentrations from area sources was the determination of what portion of the measured concentration downwind of the lagoon was attributable to that source. Generally, the data collected with the TDL depicted the periods of relatively higher emissions occurring during the day and night times which generally go undetected with the filter pack sampling.

Introduction:

Ammonia (NH₃) emissions from fertilizer applications and dairies may be significant contributors to the San Joaquin Valley, CA, air problem. Over the past five years we have been monitoring ammonia emissions from various agricultural operations in the San Joaquin Valley, California (Krauter, 2001; Krauter et al. 2001, 2002 & 2003; Potter et al., 2001). Our current research involves the use of two different ammonia sampling systems- filter packs and tunable diode lasers (TDL) (Fitz et al., 2003; Goorahoo et al., 2001; Beene et al., 2002 & 2003; Carstensen et al., 2004). Firstly, we review the technology involved in the use of active filter packs and the open path tunable diode laser (OPTDL) for monitoring ammonia emissions. Then we present examples of our research data collected to highlight the applicability of the filter packs for measuring NH₃ emissions from fertilizer applications and the TDL for monitoring diurnal and seasonal fluctuations of ammonia during various dairy management practices. We conclude the presentation with a discussion on the potential use the TDL data for validation and

assessment of the U.S. Environmental Protection Agency (EPA) model for predicting downwind concentrations from area sources.

Active ammonia sampling filter packs:

For our projects aimed at monitoring NH_3 emissions from fertilizer applications we have been using mainly the active chemical filter pack systems to collect the atmospheric NH_3 . Basically, the filter pack, sometimes referred to as a denuder, is a device that pulls air through a treated medium that changes the NH_3 to a solid. Glass filters are impregnated with 3% citric acid in 95% ethanol solution. The NH_3 forms ammonium citrate on the treated filter. In the laboratory, the micro-grams (μg) of NH_3 on the filters are determined by dissolving the ammonium in de-ionized water and measuring the concentration using Nessler reagent and a spectrophotometer. In the field, air is pulled through the ammonia filter pack using a 12V battery powered pump, and so this technique is referred to as **active sampling**, as opposed to a **passive sampling** system.

A major requirement of our research is the measurement of a vertical profile of ammonia levels to characterize the relationship between the soil/vegetation surface and the atmospheric NH_3 . To that end, multiple filter packs are mounted on a tower or mast for simultaneous sampling at various elevations. Currently, five systems with a 10m mast have been constructed and one tower of 20m was built on a trailer. The filter packs require several hours of sampling to acquire sufficient NH_3 for detection in the laboratory. Our initial work indicated a diurnal difference in atmospheric NH_3 levels so sampling is generally continuous with the filter packs changed at dawn and dusk.

Tunable Diode Laser systems:

The filter pack method for collecting atmospheric NH_3 requires several hours to collect a sample in most instances. That time period is too long to characterize short term operations such as those at dairies where a process occurring over a few minutes may produce significant NH_3 emissions that would not be detectable over the long sampling period of the filter packs (Goodrich et al., 2005).

The TDL system measures gas concentration over an open path. It consists of an integrated transmitter/receiver unit and a remote, passive retro-reflector array. The transceiver houses the laser diode source, the drive electronics, the detector module, and microcomputer subsystems. The laser light emitted from the transceiver unit propagates through the atmosphere to the retro-reflector and returns to the source, where it is focused onto a photodiode detector. A portion of the laser beam is passed through an onboard reference cell to provide a continuous calibration update.

Initially, atmospheric NH_3 was monitored in the laboratory using a TDL for open-path spectroscopy. Presently, we utilize both fixed and portable OPTDL systems. The fixed system is installed in a trailer and has been used at field sites for short term, real-time monitoring of NH_3 . When testing and installation is completed, the system will enable NH_3 to be monitored simultaneously on five paths at distances up to 500m from the laser source. There are small TDL units that are also available for portable, field monitoring of one gas on a single path. These are proven field units that are an EPA approved monitoring method for a variety of gasses.

Meteorology systems:

From the data collected with both the filter pack and TDL systems, it is possible to determine the mass of NH_3 in a known volume of air. The significance of that concentration depends upon the wind speed, which can be quite variable near the soil/vegetation surface, and over dairy lagoons. Therefore, for each set of filter pack and TDL measurements we measure or calculate wind speed value for that sample height. The sampling masts and tower used for the filter packs also have anemometers mounted at most sampling points to monitor the wind profile. Hence, NH_3 levels may then be correlated with other meteorology factors the sampling systems monitor air and soil temperature, relative humidity, solar radiation and rainfall.

Emissions from fertilizer applications in cotton measured with filter packs:

Ammonia emissions were evaluated during two anhydrous ammonia fertilizer application methods from a crop of cotton (Beene et al., 2005). The first method evaluated was a side-dress application of anhydrous ammonia shanked into the soil. This sampling was conducted during two seasons and while three different rates of nitrogen fertilizer were tested. The rates included a high, low, and variable rate of the fertilizer. The variable rate of nitrogen is sensitive to the changing yield potential of the soil. The previous years yield data was used to create a fertilizer prescription map. The sampling method used during the side-dress applications were active chemical filter packs mounted on a 10 meter tower with sampling locations at .5, 1, 2, 4, and 10m. Anemometers were co-located at each sample height while temperature and relative humidity were also logged. The second application method evaluated for fugitive ammonia emissions was a water run application of anhydrous ammonia in which the fertilizer is bubbled into the head ditch of the irrigation system and allowed to flow in the field in the irrigation water. Monitoring of the water run application was done with active chemical filter packs and open path tunable diode laser during three days of the water run application. Sampling sites were directly upwind and downwind of the field in order to obtain a net downwind concentration. Results from the side-dress application indicate higher rates of anhydrous ammonia fertilizer correlating with higher amounts of ammonia emitted. Evaluation of the water run application showed an enrichment of ambient concentrations of ammonia downwind of the field.

Emissions from dairy lagoon measured with TDL:

California is the number one dairy state, producing 26 billion pounds of milk and cheese (CDFA, 2003). Most of the dairy operations in California are concentrated in the San Joaquin Valley (SJV). While the growth of this industry results in significant economic returns for the region, there is the issue of effective manure management. Major problems associated with the manure management are high solids and nutrient contents of the effluent stream, and gas production during the decomposition of manure in storage. As a result the health, environmental and economic concerns, there is a need to quantify the NH_3 emissions at dairies. Furthermore, the spatial and temporal distribution of these gases on the farm should also be investigated. A first step in obtaining these emissions is to determine real time concentrations of these gases.

In this phase of our study, conducted over 20 months, on dairies representing management practices typical of dairies in the SJV, the applicability of TDL technology in determining gas emissions at the dairies was assessed. The first four months of the project were devoted to development of methodologies and protocols for sampling the gaseous emissions in real-time.

Then for the remainder of the project duration, the lagoons and free-stall areas at these dairies were monitored for both diurnal and seasonal fluctuations in the emission of NH₃. Real time measurements of gas concentrations were correlated with Oxidation Reduction Potential (ORP), pH and dissolved oxygen (DO) of the lagoon water.

Assuming that the TDL instruments are kept within optimum operating temperature conditions, the TDL technology is suitable for detecting the gas emissions from dairy lagoons during the summer temperatures typical of the San Joaquin Valley, CA. However, during intense fog observed during the Fall and Winter seasons, the lasers fail. The TDL technology permitted the correlation of the gas fluctuations with management practices such as aeration, agitation, lane flushing, acidification and recycling of fresh water into the dairy lagoons and subsequent application to surrounding fields. Generally, as the pH of the lagoon dropped from 8.0 to 6.5, average NH₃ fluxes decreased from approximately 1.6 to 0.5 mg m⁻² s⁻¹. Overall, NH₃ fluxes decreased when the ORP was increased from -250mV to -100mV. It is essential to conduct monitoring during the fall, winter and spring seasons to assess the performance of the TDL system under these conditions, while at the same time examining any seasonal variability in the gaseous emissions

Comparison of active filter packs and TDL measurements at dairies:

Due to the fugitive nature of emissions at dairies the emissions of pollutants cannot be directly measured. Therefore in order to determine the magnitude of NH₃ emissions, ambient monitoring and modeling must be used. This requires measuring ambient concentrations precisely and then using those concentrations in a model to determine emission rates. There are several methods that can be used to determine the ambient concentration of ammonia in the air. Concurrent measurements were made in the field along with applicable meteorological data in order to use the integrated horizontal flux method as well as the EPA approved model, Industrial Source Complex-Short Term version 3, for emission factor development.

An attempt was made to use the data collected with the TDL in an EPA approved model to predict downwind concentrations from area sources. However, due to the limited number of laser units available we are currently unable to obtain simultaneous upwind and downwind concentrations. This presents the problem of determining what portion of the measured concentration downwind of a source is attributable to that source. Nonetheless, by adopting a 3-phased sampling scheme, we should be able to use the TDL data for validation and assessment of the EPA model for predicting downwind concentrations from area sources. Generally, the data collected with the TDL depicted the periods of relatively higher emissions occurring during the day and night times which generally go undetected with the filter pack sampling.

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