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Remote sensing and *in situ* measurements of methane and ammonia emissions from a megacity dairy complex: Chino, CA☆

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ABSTRACT

Methane (CH_4) and ammonia (NH_3) directly and indirectly affect the atmospheric radiative balance with the latter leading to aerosol generation. Both have important spectral features in the Thermal InfraRed (TIR) that can be studied by remote sensing, with NH_3 allowing discrimination of husbandry from other CH_4 sources. Airborne hyperspectral imagery was collected for the Chino Dairy Complex in the Los Angeles Basin as well as *in situ* CH_4, carbon dioxide (CO_2) and NH_3 data. TIR data showed good spatial agreement with *in situ* measurements and showed significant emissions heterogeneity between dairies. Airborne remote sensing mapped plume transport for ~20 km downwind, documenting topographic effects on plume advection. Repeated multiple gas *in situ* measurements showed that emissions were persistent on half-year timescales. Inversion of one dairy plume found annual emissions of 4.1×10^5 kg CH_4, 2.2×10^5 kg NH_3, and 2.3×10^7 kg CO_2, suggesting 2300, 4000, and 2100 head of cattle, respectively, and Chino Dairy Complex emissions of 42 Gg CH_4 and 8.4 Gg NH_3 implying ~200k cows, ~30% more than Peischl et al. (2013) estimated for June 2010. Far-field data showed chemical conversion and/or deposition of Chino NH_3 occurs within the confines of the Los Angeles Basin on a four to six h timescale, faster than most published rates, and likely from higher Los Angeles oxidant loads. Satellite observations from 2011 to 2014 confirmed that observed *in situ* transport patterns were representative and suggests much of the Chino Dairy Complex emissions are driven towards eastern Orange County, with a lesser amount transported to Palm Springs, CA. Given interest in mitigating husbandry health impacts from air pollution emissions, this study highlights how satellite observations can be leveraged to understand exposure and how multiple gas *in situ* emissions studies can inform on best practices given that emissions reduction of one gas could increase those of others.

1. Introduction

1.1. Methane

The important greenhouse gas methane (CH_4) has a global warming potential (or relative cumulative forcing index) of ~100 times than of carbon dioxide (CO_2) on a decade time-scale comparable to its lifetime (Myhre et al., 2013, Fig. 8.). Moreover, its abundance is predicted to increase. Meaningful regulatory approaches require accurate current and future budgets, yet uncertainties in even the former remain large (IPCC, 2013; Kirschke et al., 2013), fueling a critical need for robust CH_4 measurement approaches to accurately estimate emissions on local to global scales.

Natural CH_4 sources account for 35–50% of the total annual budget of ~550 ± 87 Tg yr^{-1} while anthropogenic sources contribute the remainder. Natural wetlands emissions contribute

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the most strongly, 177–284 Tg yr^{-1}, but are poorly constrained. Anthropogenic emissions include rice-paddies agriculture, ruminants, sewage and waste, landfills, and fossil fuel industrial (FFI) emissions (IPCC, 2013).

Microbial production underlies many anthropogenic CH_4 emissions-including landfills, rice, and ruminants. Ruminants (cattle, sheep, goats, etc.) produce CH_4 by food fermentation with total estimated emissions of 87–94 Tg yr^{-1} (IPCC, 2013), comparable to some estimates of natural gas pipeline losses, at 85–105 Tg yr^{-1} (IPCC, 2013), though recent studies suggest petroleum-related emissions may be underestimated by a factor of 1.5–2 (Miller et al., 2013). Significant ruminant emissions arise from diverse nations globally, with India maintaining the largest ruminant population (Chhabra et al., 2013).

Atmospheric gas concentration depends on the balance between sources and sinks. CH_4's atmospheric lifetime is ~8.5–9 yr in mid-latitudes, constrained primarily by reaction with the hydroxyl (OH) (Sonnemann and Grygalashvyly, 2014; Voulgarakis et al., 2013). Atmospheric CH_4 isotopic modeling suggests OH oxidation has increased ~5% since 1980, decreasing CH_4 lifetimes (Lassey and Ragnauth, 2010). There is a feedback with OH concentration being affected by increasing CH_4 concentrations. However, the sink from terrestrial uptake was estimated recently to be higher than previously considered (Fernandez-Cortes et al., 2015), suggesting even shorter lifetimes are likely.

1.2. Ammonia

Ammonia (NH_3) is an important contributor to the atmospheric nitrogen budget and is the most abundant form of atmospheric gas-phase reduced nitrogen (Heald et al., 2012) with significant indirect climate implications (due to its important role in fine aerosol formation) as well as impacts on air quality and human health (Paulot and Jacob, 2014). The primary NH_3 sources are agricultural (Aneja et al., 2000), although vehicular emissions can dominate in urban areas (Schiferl et al., 2014). Reis et al. (2009) suggest 1.8% and 7% for European and U.S. vehicular NH_3 emissions, respectively. Overall anthropogenic sources now overwhelm natural contributions to the nitrogen cycle (Galloway et al., 2008), with ecosystem implications from excess nitrogen input into sensitive ecosystems including eutrophication. Dry deposition can contribute from 1 to 40% of nitrogen input in different coastal areas (Howarth, 2008).

There is significant variability in NH_3 spatial emissions and resultant concentrations on a range of scales due to the importance of husbandry and agricultural practices that differ between facilities/farms, regions, and nations, as well as within a facility/farm. Husbandry NH_3 emissions are strongly seasonal, given that volatilization from animal wastes is temperature dependent and because fertilizer application occurs on a seasonal basis (Hertel et al., 2011). For example Gilliland et al. (2003) found an increase of ~80% for U.S. emissions between January and July, while Warner et al. (2016) found an increase of ~150% for the northern hemisphere based on Atmospheric InfraRed Sounder (AIRS) long-term data. Gilliland et al. (2003) also notes uncertainty in U.S. NH_3 emissions because husbandry practices differ between the U.S. and Europe with the EDGAR emission inventory database (v4.2) relying on European studies. EDGAR attributes globally 58% to agricultural soil emissions (fertilizer), 21% to animal wastes, and 16% from fires (European Commission, 2009). Given that dairy production and non-cattle livestock are expected to increase in the U.S (Wescott and Trostle, 2007). and globally, husbandry NH_3 emissions likely will increase, particularly in the tropics (Galloway et al., 2008).

NH_3 concentrations decrease rapidly with altitude, particularly above the surface boundary layer, generally falling to well below 1 ppb at 900 hPa in moderately polluted environments. In low pollution environments, surface values are low, less than 0.1 ppb (Schiferl et al., 2014). The exception is areas of intensive husbandry, where concentrations at 900 hPa can be 1–10 ppb (Schiferl et al., 2014).

The lifetime of NH_3 is far shorter than that of CH_4, ranging from as fast as 1 h (Baek et al., 2004) to 1 day (Pinder et al., 2008) to as long as 5 days (Pinder et al., 2008), while the lifetime of ammonium (NH_4^+) aerosols is ~1 week (Pinder et al., 2008; Pye et al., 2009). NH_3 loss occurs by dry (or wet) deposition and by gas-to-particle conversion – e.g., in the presence of sulfate from sulfur dioxide (SO_2) or nitric acid - from nitrogen oxides (NO_X) oxidation, forming NH_4^+ salt aerosols (Pinder et al., 2008). These conversions are bidirectional with the gas-aerosol partitioning depending on temperature, humidity, and the availability of sulfur oxides (SO_X) and NO_X (Dawson et al., 2007). Regulatory reductions in SO_2 and NO_X have shifted the aerosol formation pathways and increased the importance of NH_3 (Heald et al., 2012).

The gas-particle phase partitioning is strongly temperature and humidity dependent with warmer temperatures shifting the balance towards the gas phase, and thus partitioning varies seasonally (Stelson and Seinfeld, 1982). Additional complexity arises because dissociation depends on particle composition (Nowak et al., 2010). Depending on aerosol size, equilibration can be very fast, sub-hourly for submicron particles (Pye et al., 2009); however, this presumes sufficient oxidants for conversion. The relatively long lifetime of NH_4^+ allows transport and impacts over thousands of kilometers, while NH_3 largely affects regions nearby sources (Hertel et al., 2011).

1.3. Health impacts from ammonia

To address the environmental and health impacts associated with husbandry, the EPA is planning new regulations under the Clean Air Act. In a nationwide longitudinal study, Sneeringer (2009) found a 7.4% increasing in infant mortality associated with respiratory diseases on a national basis, indicative of an airborne pollution mechanism. Contributors include NH_3, hydrogen sulfide (H_2S), a range of volatile organic carbon emissions, and aerosols (Li and Moore, 2007). Thus, NH_3 from husbandry is both an indicator of the presence of other agents with health risk factors, a cause of health impacts itself in high enough levels, and a precursor for acid aerosol formation which have their own health impacts.

NH_3 at high concentrations has a common history of health impacts from accidental releases due to its widespread use (Weisskopf et al., 2003) with a US industrial exposure limit of 25 ppm (Lindgaard-Jørgensen and Bender, 1992). NH_3 is the most common cause of industrial fatalities in the US (Anderson, 2015). Like H_2S, NH_3 is a vasorelaxant (Li and Moore, 2007; Yang et al., 2008) that can cause central nervous system disorders including progressive neurological failure and coma for high exposures (Kilburn, 2000). Eye irritation from NH_3 can occur at 4 ppm. For comparison, typical NH_3 concentrations range from 5 to 70 ppm in animal confinement facilities (Rice et al., 2006).

There is extensive evidence that fine (PM10) aerosols, such as formed from NH_3, are significant causes of cardiopulmonary disease for both short-term and long-term exposure with high mortality rates (Pope III and Dockery, 2006 and studies reviewed therein). Aerosol health impacts occur by a range of mechanisms including inflammation, platelet activation, vasoconstriction, and depression of defenses against infection (Chow et al., 2006).

1.4. Study motivation and overview

Husbandry emits both NH_3 and CH_4, providing an opportunity to use NH_3 as a fingerprint to discriminate husbandry CH_4 plumes