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An empirical inferential method of estimating nitrogen deposition to Mediterranean-type ecosystems: the San Bernardino Mountains case study

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ABSTRACT

The empirical inferential method (EIM) allows for spatially and temporally-dense estimates of atmospheric nitrogen (N) deposition to Mediterranean ecosystems. This method, set within a GIS platform, is based on ambient concentrations of NH_3, NO, NO_2 and HNO_3; surface conductance of NH_4^+ and NO_3^-; stomatal conductance of NH_3, NO, NO_2 and HNO_3; and satellite-derived LAI. Estimated deposition is based on data collected during 2002–2006 in the San Bernardino Mountains (SBM) of southern California. Approximately 2/3 of dry N deposition was to plant surfaces and 1/3 as stomatal uptake. Summer-season N deposition ranged from <3 kg ha^{-1} in the eastern SBM to ~60 kg ha^{-1} in the western SBM near the Los Angeles Basin and compared well with the throughfall and big-leaf micrometeorological inferential methods. Extrapolating summertime N deposition estimates to annual values showed large areas of the SBM exceeding critical loads for nutrient N in chaparral and mixed conifer forests.

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1. Introduction

Elevated deposition of reactive nitrogen (N) has serious ecological effects in forests and other ecosystems such as water contamination or biodiversity changes that include shifts in lichen communities or invasion of alien plant species (Galloway et al., 2003; Fenn et al., 2011; Greaver et al., 2012). In the Mediterranean ecosystems of California, deposition of N is dominated by dry deposition (Bytnerowicz and Fenn, 1996). Forests and other ecosystems downwind of large air pollution source areas, such as the Los Angeles Basin or Central Valley of California, experience high concentrations of N compounds including nitrogen oxides (NO_x), ammonia (NH_3), nitric acid (HNO_3), particulate nitrate (NO_3^-) and ammonium (NH_4^+) as well as various organic compounds (Bytnerowicz and Fenn, 1996). Elevated N deposition is also an integral part of a complex of multiple stressors affecting the health of California forests (Grulke et al., 2009).

Many factors can potentially regulate dry deposition to vegetation (Lovett, 1994). The most important factors controlling dry N deposition to vegetation are ambient concentrations of N compounds, physicochemical conditions controlling their deposition velocities, canopy characteristics and prevailing micrometeorology (Hertel et al., 2011). Highly reactive and water soluble NH_3 and HNO_3 are characterized by high deposition velocities and are readily deposited to leaf surfaces and plant canopies (Hanson and Lindberg, 1991). Gaseous N pollutants are also taken up through stomatal pores followed by their dissolution in the apoplast. This process is controlled by the degree of stomatal aperture and by gas concentrations in the sub-stomatal cavity (Massad et al., 2010). Additionally, HNO_3, due to its reactivity with cuticular waxes, may be transported into the leaf interior via transcuticular transport (Bytnerowicz et al., 1999; Padgett et al., 2009). Nitrogen dioxide (NO_2), and especially nitric oxide (NO), are less water soluble than NH_3 and HNO_3 and their deposition fluxes to vegetation are thought to be controlled chiefly by stomatal uptake (Saxe, 1986; Raivonen et al., 2009). For NH_3, the difference between

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concentrations in ambient air and the stomatal cavity determines the NH_3 compensation point and direction of the NH_3 flux. When ambient concentrations of NH_3 are higher than in the stomatal cavity, plants act as a sink, and when this gradient is reversed, plants function as a source (Massad et al., 2010; Raivonen et al., 2009).

While other gaseous N compounds, such as peroxyacetyl nitrate (PAN), may also contribute to atmospheric N inputs (Zhang et al., 2009), most of N dry deposition is caused by NH_3, HNO_3, NO, and NO_2 as well as surface deposition of particulate nitrate (NO_3^-) and ammonium (NH_4^+) (Hanson and Lindberg, 1991).

Reliable, fine-scaled, and time-specific information on N deposition is essential for understanding its potential effects on ecosystems. However, current approaches used to accomplish this goal in arid and semi-arid zones are inadequate, mainly due to high uncertainty in estimates of dry deposition fluxes. The CMAQ (Community Multi-scale Air Quality) modeling system is the most commonly used in the United States to estimate N deposition. CMAQ has been used at larger (regional) scales with a typical resolution of 36 × 36 km, and more recently at 12 × 12 km for the U.S. (http://www.epa.gov/AMD/Research/RIA/cmaq.html). CMAQ has also been run at a finer resolution of 4 × 4 km in California (Fenn et al., 2010; Tonnesen et al., 2007). However, even the finer resolution simulated deposition results are often not adequate for the landscape-level spatial and temporal detail of N deposition information required for understanding potential ecological impacts. Simulated deposition models provide useful outputs for broad-scale studies or analyses, but are inadequate for site-specific or more focused ecosystem response studies. These limitations also apply to the new hybrid TDEP model (Schwede and Lear, 2014) which improves the accuracy of CMAQ in regard to N deposition estimates, especially for chemically-reduced forms, by merging ambient monitoring data with modeled data. Both CMAQ and TDEP are based on the 12 × 12 km grid scale and thus have limited capacity to simulate orographic effects on deposition in montane regions (Dentener et al., 2014; Hertel et al., 2011).

Throughfall analysis is a widely-used technique, providing a lower-bound estimate of total N deposition to plant canopies (Lovett and Lindberg, 1993). This method has been widely used in mesic conditions giving reasonable estimates of N deposition in forests and other ecosystems. However, in the Mediterranean climate this method has some major limitations related to the unpredictable and often insufficient precipitation required for removal of canopy-intercepted N. Consequently, during prolonged dry periods no throughfall samples are collected until the next precipitation event. It isn't known to what extent throughfall underestimates total N deposition under these conditions (Fenn et al., 2005; Lovett and Lindberg, 1993). In addition, throughfall measurements do not account for N gases taken up by vegetation via stomatal uptake (Draaijers et al., 1997) or by other canopy retention mechanisms (Lovett and Lindberg, 1993).

In estimates of dry N deposition to uniform vegetation canopies, such as lowland forests and forest plantations, micrometeorological methodologies, such as eddy correlation, aerodynamic gradient method, eddy accumulation or mass balance techniques, have been widely used (Fowler et al., 2009). However, use of such methods for extended periods or over large areas is impractical because of their complexity and instrumental requirements (Baldocchi et al., 1988). In addition, these methodologies cannot be applied in complex topography with non-uniform vegetation coverage. For such conditions inferential methods have been used to evaluate dry deposition fluxes of various elements important to ecosystems (Hanson and Lindberg, 1991; Lovett, 1994). In this approach fluxes are determined as the product of concentration and the deposition velocity of a given gaseous compound (Baldocchi et al., 1988).

Passive samplers based on diffusion of gases to the collecting media provide valuable pollutant concentration information needed for inferential estimates of N dry deposition at the landscape level (Bytnerowicz et al., 2000; Krupa and Legge, 2000). Determinations of NO, NO_x and NH_3 concentrations across the landscape have been successfully conducted using passive samplers in California and other parts of the country (Bytnerowicz et al., 1999; Roadman et al., 2003). Passive samplers for HNO_3 (Bytnerowicz et al., 2005), have been used in recent monitoring campaigns in remote areas of California, Alaska, and northern Alberta (Bytnerowicz et al., 2010).

In the inferential approach for estimating N fluxes, it is important to use reliable values for conductance (leaf, branch level) or deposition velocity (canopy level) for the major dry-deposited compounds. These values for specific N gases are available in the literature and are mainly based on various micrometeorological studies (Hanson and Lindberg, 1991; Zhang et al., 2003, 2009). Branch rinsing techniques have been used for removal of the surface deposited ions and their vegetation fluxes (Lovett and Lindberg, 1984; Bytnerowicz et al., 1987; Hanson and Lindberg, 1991; Watanabe et al., 2008). These methods cannot distinguish sources of the surface-deposited NO_3^- (HNO_3 or particulate NO_3^-), nor NH_4^+ (NH_3 or particulate NH_4^+) (Dasch, 1989) and may underestimate deposition to foliar surfaces due to the trans-cuticular uptake or translocation processes of the deposited chemical species (Garten and Hanson, 1990). However, despite these deficiencies the branch-rinsing method may be very useful for development of in-canopy deposition models (Hanson and Lindberg, 1991). These include an inferential method developed for mixed conifer forest stands in southern California to determine surface fluxes and also internal uptake of major N gases (Bytnerowicz et al., 1999). Consequently, research presented here is a further refinement and improvement of this approach, applicable to the landscape level. With this approach, gaseous concentrations of reactive N are measured with passive samplers across a landscape-scale monitoring network. Atmospheric N deposition is calculated within a GIS platform using: time-averaged concentrations of NH_3, NO, NO_2, and HNO_3; empirically-obtained surface deposition conductance and literature-based stomatal conductance values for the key plant species representative of various vegetation types in the study area; and layers of vegetation cover and leaf area index. Others have previously applied passive sampler concentration data for N pollutants in the inferential approach combined with various estimates of particulate and wet N deposition (Allen et al., 2011; Schmitt et al., 2005).

The objectives of the study were: (1) Describe a new approach based on empirical data and a GIS-based inferential platform to estimate atmospheric N deposition to forests and other ecosystems in Mediterranean areas characterized by complex topography; (2) Provide fine-resolution (landscape level) estimates of deposition applicable for understanding their potential biological effects in terrestrial ecosystems; (3) Compare results of the described methodology with other approaches such as the big-leaf inferential model, throughfall and the hybrid TDEP model, and; (4) Evaluate exceedances of critical loads for sensitive indicators of nutrient N deposition.

2. Methods

2.1. Study area

The monitoring network located within the San Bernardino Mountains of southern California consisted of 13 sites in 2002 and 2006 and 17 in 2003–2005. Distribution of the monitoring sites from the 2006 season for which deposition maps were developed is