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Isotopic fingerprinting of atmospheric nitrogen and sulfur using lichens (*Cladia retipora*) in Tasmania, Australia

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ABSTRACT

Increases in global anthropogenic emissions are far reaching, and are a concern even in remote areas. Tasmania, Australia is an island state that hosts the only Southern Hemisphere premier Baseline Air Pollution Station as part of the World Meteorological Organization-Global Atmosphere Watch network. Despite Tasmania's importance as a baseline location, little is known about atmospheric nitrogen (N) and sulfur (S) deposition and sources across the state. Here we investigate total N and S content and isotopic compositions ($\delta^{15}N$, $\delta^{34}S$) in the lichen *Cladia retipora* as a bio-indicator to identify whether atmospheric N and S deposition in Tasmania is affected by anthropogenic pollution. Both TN and TS were extremely low in all 66 samples collected across the state, averaging 0.29 ± 0.28% and 0.03 ± 0.05%, respectively. The average $\delta^{15}N$ value was −2.8 ± 1.9‰ and there was no correlation with TN, but values were highest towards the denser populated SE of Tasmania. Lichens collected from sites within 500 m of salt marshes revealed a strong local source of microbially-reduced S as indicated by $\delta^{34}S$ values as low as −21.9‰. All other lichen samples had a mean value of $\delta^{34}S$ value of 13.7 ± 2.2‰, indicating mixing of marine biogenic S and anthropogenic S. This study represents the first baseline study of atmospheric N and S in *C. retipora* across Tasmania, and demonstrates the suitability of lichen bio-monitoring for future studies in this region.

1. Introduction

Global emissions of fixed nitrogen as of ~2006 were approximately four times the levels estimated before the industrial revolution, which has subsequently led to increased deposition of atmospheric nitrogen (N) into the terrestrial biosphere (Phoenix et al., 2006). The consequences of increasing N deposition are diverse, including acidification and eutrophication. Gaseous anthropogenic N emissions include nitrogen oxides (NO_x), nitrous oxide (N_2O) and ammonia (NH_3) that may cause changes in soil pH, biodiversity, plant health, and eutrophication (Bobbink et al., 2010; Doney et al., 2007; Vitousek et al., 1997). Excess N in the environment was estimated in 2011 to cost the European Union between €70 billion/yr and €320 billion/yr, in terms of increased algal blooms, and excess nitrate and reactive N (Sutton et al., 2011). Future rates and distributions of N deposition are predicted to more than double from 2006 rates by 2050, severely harming global floristic diversity (Phoenix et al., 2006) with attendant increased economic costs.

Sulfur emissions are of similar concern. Anthropogenic sulfur (S) emissions (e.g. SO_2) and its oxidation in the atmosphere will lead to atmospheric H_2SO_4 formation (Seinfeld and Pandis, 2006). Aquatic and terrestrial ecosystems are then acidified when the dissociated members dissolve upon deposition (Doney et al., 2007). S emission rates have recently undergone a reversal, increasing until the late 1980s and then stable to declining since the early 1990s (Stern, 2006). Despite declines in deposition rates reported for e.g. North America and Europe (Stoddard et al., 1999), little is known about N and S deposition in Oceania in general and Australia in particular. Atmospheric N and S measurements taken at the Cape Grim Baseline Atmospheric Pollution Station (CGBAPS) on the north-western coast of Tasmania have been reported predominantly in the 1980s and 1990s (Ayers et al., 1986, 1997; Ayers and Ivey, 1988; Ayers et al., 1997; Andreae et al., 1999; Mace et al., 2003). Reported data include levels of methanesulfonate, dimethyl sulfide, SO_2, and aerosol SO_4, but no conclusions were made regarding atmospheric deposition rates (wet and dry) that could be compared to elsewhere in the World. More recent but sparse data including NO_2 and SO_2 measurements were reported by the Tasmanian Environmental

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Protection Agency (Hibberd, 2008), but assessments focus on particulate matter emissions derived from biomass burning. The Cape Grim station recently recorded CO_2 levels exceeding 400 ppm for the first time, which is significant because the sampled air at Cape Grim is considered to be representative of a large area of the Southern Hemisphere, and is considered unaffected by regional pollution sources (CSIRO, 2016). Despite Tasmania's ongoing clean air image due to its remote location, National Pollution Inventory entries are incomplete and no efforts have been made to measure nitrogen and sulfur deposition rates in the state to verify pristine atmospheric conditions.

Tasmania is an island state of Australia, located approximately 240 km south of the Australian mainland (Fig. 1). The main island covers more than 68 000 km, and has a population of approximately 500 000. Tasmania is characterized by rugged topography, extensive forests, and a temperate climate (Kottek et al., 2006; Davies, 1965). It features the mountainous Central Highlands area in the central-western parts of the state, the flat agricultural Midlands in the central-east, dense temperate forests in the south-west, and temperate rain forests in the north-west. Many parts of Tasmania are remote with difficult access, making direct measurements of atmospheric deposition expensive, logistically challenging, and time consuming.

Lichens are excellent bio-indicators of air pollution that have been used for more than 40 years (Krouse, 1977; Balaguer and Manrique, 1991; Batts et al., 2004; Barros et al., 2015), particularly in isotope studies for source determination (Proemse and Mayer, 2012; Barros et al., 2015) and in remote areas where air quality measurements using direct samplers are difficult to deploy and maintain (Batts et al., 2004; Boltersdorf and Werner, 2014).

Lichens efficiently take up compounds from gases, wet, and dry deposition, providing an opportunity to monitor atmospheric S and N pollution (Balaguer and Manrique, 1991; Gries et al., 1997; Wadleigh, 2003; Dahlman et al., 2004; Carvalho and Freitas, 2011). Atmospheric compounds including SO_2, H_2S, NH_3, NH_4, and NO_x have a profound effect on lichens (Dahlman et al., 2004; Hawksworth and Rose, 1970; van Dobben and ter Braak, 1999, Krupa, 2003; Loppi and Frati, 2006; Loppi and Nascimbene, 2010; Tozer et al., 2005), but particulate matter (e.g. PM2.5) may also affect elemental composition (Carvalho and Freitas, 2011). Therefore lichens can provide excellent bio-monitoring tools regardless of the form of pollutant.

The objective of this study was to use samples of *C. retipora* as an indicator of atmospheric N and S deposition across Tasmania to assess its suitability for baseline data as indicated by the Cape Grim Baseline Atmospheric Pollution Station. Using lichens as bio-indicators allowed the inclusion of many locations that are infeasible to study using traditional atmospheric deposition sampling techniques. Lichen samples were analyzed for total nitrogen (TN), total sulfur (TS), and the isotopic compositions of N ($\delta^{15}N$) and S ($\delta^{34}S$) to identify possible sources of atmospheric N and S deposition in Tasmania.

2. Material and methods

The “coral lichen”, *Cladia retipora* (Labill.) Nyl. is a clathrate fruticose lichen that is widespread throughout Tasmania (Jarman et al., 1988). Such lichens with a green-algal phycobiont (Green et al., 1997) are incapable of fixing N. Lichens are incapable of absorbing nutrients from the substrate they grow on. Therefore, their N content is entirely determined by their uptake of atmospheric N compounds other than N_2.

C. retipora was sampled from Tasmanian locations ranging between sea level and 1250 m elevation, from many different habitats including temperate forests, alpine and subalpine heath, and coastal biomes. A total of 66 samples from 53 sites were sampled by investigators and volunteers between November 2015 and March 2016 (Fig. 1).

C. retipora has highly variable growth rates, from <1 mm/yr up to a few cm/yr in radial extension, so it is impossible to accurately determine the age of each specimen without a careful study of each individual habitat (G. Kantvilas, personal communication, 2016). Therefore, we make no direct assumptions about age, and sampled from large patches of lichen that represent at least a year's worth of growth. Each sample was removed, cleaned of physical debris, and dried at 40 °C. The samples were then homogenized by pulverizing with mortar and pestle and weighed into tin cups; approximately 10 mg for N analysis and 15 mg for S analysis. We analyzed full lichen thalli from apex to base to obviate internal differences in N composition resulting from internal cycling (Ellis et al., 2003).

The samples were analyzed for their total N content (TN), total S content (TS), N isotopic composition ($\delta^{15}N$), and S isotopic

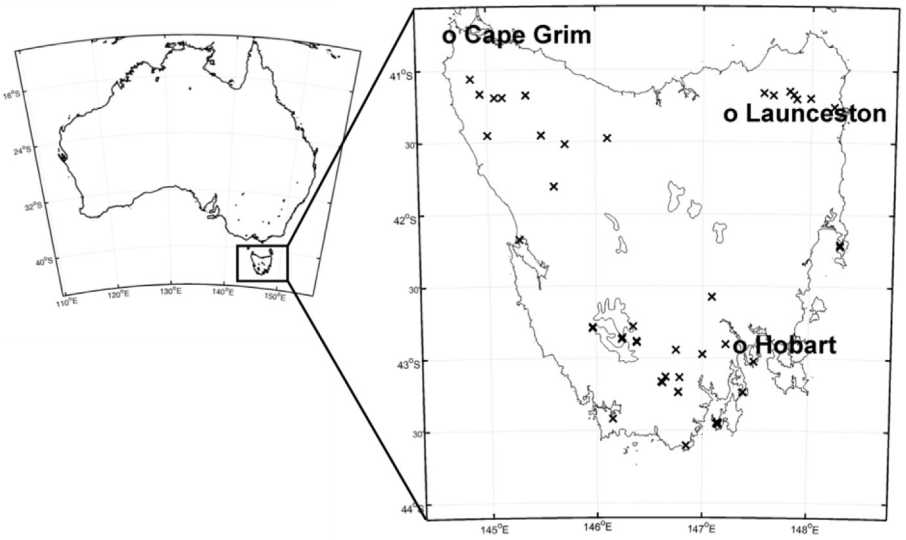

Fig. 1. Sampling locations of *C. retipora* in Tasmania, Australia's island state. The Cape Grim Baseline Atmospheric Pollution Station is located at Cape Grim. Hobart and Launceston are Tasmania's largest urban centres.