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Monitoring atmospheric nitrogen pollution in Guiyang (SW China) by contrasting use of *Cinnamomum Camphora* leaves, branch bark and bark as biomonitors☆

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ABSTRACT

Moss (as a reference material) and camphor (*Cinnamomum Camphora*) leaf, branch bark and bark samples were systematically collected across an urban-rural gradient in Guiyang (SW China) to determine the efficacy of using these bio-indicators to evaluate nitrogen (N) pollution. The tissue N concentrations (0.13%–2.70%) and $\delta^{15}N$ values (−7.5‰ to +9.3‰) of all of these bio-indicators exhibited large spatial variations, as they recorded higher values in urban areas that quickly decreased with distance from the city center; moreover, both soil N concentrations and soil $\delta^{15}N$ values were found no significant differences within each 6 km from the urban to the rural area. This not only suggests that the different N uptake strategies and variety of N responses of these bio-indicators can be reflected by their different susceptibilities to variations in N deposition but also reveals that they are able to indicate that urban N deposition is mostly from traffic and industry (NO_x-N), whereas rural N deposition is mainly from agriculture (NH_x-N). Compared to previously collected urban moss and camphor leaf samples, the significantly increased $\delta^{15}N$ values in current urban moss and camphor leaf samples further indicate a greater contribution of NO_x-N than NH_x-N to urban N deposition. The feasibility of using the N concentrations and $\delta^{15}N$ values of branch bark and bark as biomarkers of N deposition thus was further confirmed through the comparative use of these bio-indicators. It can be concluded that vascular plant leaves, branch bark and bark can be used as useful biomonitoring tools for evaluating atmospheric N pollution. For further study, quantitative criteria for the practical use of these bio-indicators in response to N deposition should be developed and the differences in the $\delta^{15}N$ values of different plant parts should also be considered, particularly in urban environments that are severely disrupted by atmospheric pollution.

1. Introduction

The high density of traffic, population and industries have contributed massive inputs of reactive N to the atmosphere; therefore, many regions of China are experiencing intense air pollution, which has been further exacerbated by enhanced agricultural activities (Liu et al., 2011; Kan et al., 2012). N pollutants emitted into the atmosphere can be removed from the atmosphere by wet or dry deposition to lakes, soil and plants (Goulding et al., 1998; Zhang et al., 2010), which can lead to lacustrine and estuarine eutrophication, toxic metal activation, soil acidification, an imbalance in the availabilities of cations, changes in the biodiversity of terrestrial ecosystems, and the degradation of human health (Schulze, 1989; Galloway et al., 2004; Richter et al., 2005; Stevens et al., 2009). However, determining the origin of N pollutants and investigating the level of atmospheric N pollution is extremely difficult, as N emissions are usually derived from different anthropogenic sources and the deposition of N includes a variety of N compounds that exist in aerosols, gas phases, and precipitation. In contrast, bio-monitors represent an inexpensive, effective and reliable method of evaluating atmospheric N pollution.

Vegetation is one of the most important biological sinks for

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atmospheric N, which occurs through the processes of both dry and wet deposition. It is generally accepted that the highly consistent responses of plant tissues (e.g., mosses, lichens, vascular plant leaves) to increased atmospheric N inputs yield significantly higher tissue N concentrations (Hicks et al., 2000; Pitcairn et al., 2003; Liu et al., 2013). Mosses, which are mainly reliant on atmospheric N inputs as their source of N, have been more frequently used in studies of atmospheric N deposition than vascular plant leaves. The robust correlation between moss N concentrations and total atmospheric N deposition has been established in field studies (Xiao et al., 2010a). Additionally, the fact that the N concentrations of some vascular plant leaves (e.g., *Calluna vulgaris*, *Nardus stricta* and *Deschampsia flexuosa*) increase linearly with N deposition was also observed by Hicks et al. (2000) and Pitcairn et al. (2001). These bio-indicators (especially mosses) can therefore be suitable for determining the levels of regional and even national N deposition. Differently, the outermost tree bark of a tree trunk is primarily used to investigate local or regional atmospheric heavy metal pollution because of its constant exposure to the atmosphere (Bellis et al., 2001; Saarela et al., 2005; Suzuki, 2006). Schulz et al. (1997) determined that a relationship exists between the NO_3^- and NH_4^+ concentrations in pine tree barks and throughfall concentrations, such that the concentrations of oxidized and reduced N species in pine tree barks can be used to quantify throughfall rates. This indicates that bark and branch bark N concentrations may be closely linked to atmospheric N deposition. In addition, the findings obtained by Mitchell et al. (2005) and Boltersdorf et al. (2014) also suggested that tree bark can represent another resource with which to assess N deposition. However, studies of the use of bark and branch bark N concentrations as indicators of N deposition are still quite limited compared to those of mosses and tree leaves, which demonstrates the urgent and important need to study the susceptibility of bark and branch bark to increased N deposition.

It has been proposed that measuring N isotopic compositions in plants and soils via a single sampling (so that the system would not be disturbed by adding a ^{15}N tracer) might not only offer instantaneous information about N sources but may also yield the advantage of providing insights into the N cycling history of a region (Robinson, 2001; Pardo et al., 2007). Additionally, the isotopic compositions of atmosphere-derived N have been increasingly used to identify the potential N sources of inputs into various plant and soil environments (Evans and Ehleringer, 1993; Durka et al., 1994; Pearson et al., 2000; Redling et al., 2013). As well known, NO_x-N and NH_x-N are the two main sources for N pollution, which can be distinguished isotopically because higher $\delta^{15}N$ values were generally reported for NO_x compared to NH_x (Table S1). Therefore, results from many literature have shown that the analysis of $\delta^{15}N$ values in moss tissues can be used to distinguish the contributions of various N emission sources to regional atmospheric N deposition, because the N isotopic effects during N uptake are very low or even absent, such that the effectiveness of N emission reductions can be assessed (Bragazza et al., 2005; Solga et al., 2005; Pitcairn et al., 2006; Xiao et al., 2010b). Our knowledge of the use of vascular plants to evaluate atmospheric N pollution, by contrast, remains relatively poor, because many complex factors that affect $\delta^{15}N$ values in vascular plant tissues should be taken into account, namely, differences in N sources (e.g., soil organic N, soil NH_4^+, soil NO_3^-, and atmospheric N), root depth, plant mycorrhizal status, the transpiration efficiency of net N uptake, the influence of canopies, and fractionation in soil-plant systems (Högberg, 1997; Michelsen et al., 1998; Evans, 2001; Cernusak et al., 2009). Although this complexity does exist, several previous studies have revealed that the $\delta^{15}N$ values of vascular plant leaves can be affected by N deposition (Jung et al., 1997; Köchy and Wilson, 2001; Stewart et al., 2002; Kuang et al., 2011). Previous studies that have used the N isotopic compositions of vascular plant leaves as indicators of atmospheric N pollution have mainly focused on coniferous trees in non-urban ecosystems (mainly forest ecosystems) (Gebauer et al., 1994; Ammann et al., 1999; Bukata and Kyser, 2007; Kuang et al., 2011); however, thus far, relatively little attention has been paid to the response of vascular plants on atmospheric N pollution in urban environments. Bark, as a passive bio-indicator can directly adsorb N compounds or other pollutants from the atmosphere or from throughfall or stemflow. This characteristic of bark would cause a change in the chemical composition of its surface layer. Such changes can thus be used to evaluate the extent to which a given region has been subjected to atmospheric pollution (Poikolainen, 1997; Schulz et al., 2001; Suzuki, 2006). Although the determination of pine bark $\delta^{15}N$ values has been successfully applied in indicating NH_3 sources from agricultural activities (Schulz et al., 2001; Boltersdorf et al., 2014), a better understanding of the impacts of atmospheric N deposition on bark and branch bark $\delta^{15}N$ is still required. In particular, different bio-indicators have different N acquisition pathways and mechanisms, it implies the existence of their different N responses following the influence of N pollution. But until now, no study has systematically investigated the differences of $\delta^{15}N$ value variation in different plant parts (e.g., leaves, branch bark and bark) or different bio-indicators (e.g., leaves, branch bark, bark and mosses) in response to atmospheric N pollution.

This study thus utilizes mosses, leaves, branch bark and tree bark as indicators of N deposition; furthermore, through the determination of N concentrations and $\delta^{15}N$ values in these four bio-indicators, which were collected across an N deposition gradient in the Guiyang area, their abilities to reflect atmospheric N pollution were compared. The questions that were further discussed included the following: (1) Whether the evaluation conclusion of spatial distribution of N deposition in the study area is consistent via N concentration data of the four bio-indicators? (2) Are there any differences in the $\delta^{15}N$ values between these bio-indicators; if so, what affects them? (3) Does N deposition leave a recognizable N isotopic signal in bark and branch bark? (4) What are the main sources of N deposition in the current Guiyang area, and has the importance of different N pollution sources changed over time, according to the $\delta^{15}N$ values in these bio-indicators?

2. Materials and methods

2.1. Study area

Guiyang city of southwest China is situated in a wide karst valley basin with an average altitude of 1250 m. The city is characterized by a subtropical monsoon climate with an annual mean temperature of 15.3 °C and an annual mean rainfall of 1174.7 mm; the prevailing wind direction is southeast in the summer (Guiyang Environmental Protection Bureau, 2006). The main lithological feature in this study area was classified as carbonate; the soil is dominated by strongly weathered, acidic yellow soil, which records high aluminium concentrations and low base saturation (Larssen et al., 1998; Han et al., 2011).

The city center, which is located in the southern region of Yunyan and the northern region of Nanming, contains more than 100,000 vehicles and has a population density of 30,000/km^2 (Li et al., 2012). The total motor vehicle population in the city increased by 344%, from 225,400 in 2005 to 1,000,000 in 2015 (He, 2013; Traffic Management Bureau of Guiyang, 2016). Vehicles are regarded to represent the main source of NO_x-N pollution. A typical example is that the NO_x from vehicle emissions in Guiyang in 2010 accounted for 56.2% of total NO_x emissions (36.6 kt yr^{-1}) (He, 2013; Tian et al., 2013). In the past, low rates of wastewater treatment

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