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Direct effect of acid rain on leaf chlorophyll content of terrestrial plants in China

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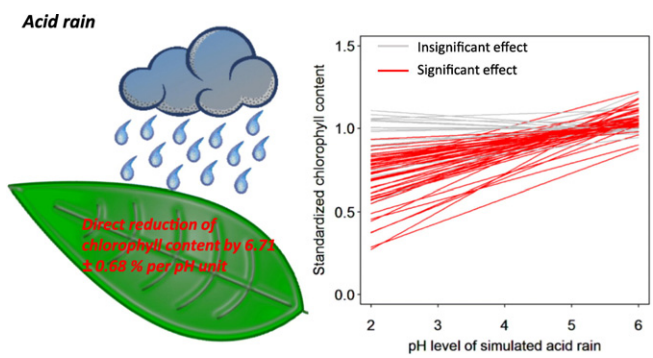
HIGHLIGHTS

- The direct effect of acid rain on leaf chlorophyll content was assessed.
- Acid rain reduced leaf chlorophyll content on average by 6.7% per pH unit.
- The effect showed no difference across calcicoles, ubiquists and calcifuges.
- Deciduous species were more sensitive to acid rain than evergreen species.
- Vegetables and fruit trees were more sensitive to acid rain than other types.

GRAPHICAL ABSTRACT



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ABSTRACT

Anthropogenic emissions of acid precursors in China have resulted in widespread acid rain since the 1980s. Although efforts have been made to assess the indirect, soil mediated ecological effects of acid rain, a systematic assessment of the direct foliage injury by acid rain across terrestrial plants is lacking. Leaf chlorophyll content is an important indicator of direct foliage damage and strongly related to plant productivity. We synthesized data from published literature on experiments of simulated acid rain, by directly exposing plants to acid solutions with varying pH levels, to assess the direct effect of acid rain on leaf chlorophyll content across 67 terrestrial plants in China. Our results indicate that acid rain substantially reduces leaf chlorophyll content by 6.71% per pH unit across the recorded plant species. The direct reduction of leaf chlorophyll content due to acid rain exposure showed no significant difference across calcicole, ubiquist or calcifuge species, implying that soil acidity preference does not influence the sensitivity to leaf injury by acid rain. On average, the direct effects of acid rain on leaf chlorophyll on trees, shrubs and herbs were comparable. The effects, however varied across functional groups and economic use types. Specifically, leaf chlorophyll content of deciduous species was more sensitive to acid rain in comparison to evergreen species. Moreover, vegetables and fruit trees were more sensitive to acid rain than other economically used plants. Our findings imply a potential production reduction and economic loss due to the direct foliage damage by acid rain.

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1. Introduction

Accelerated emissions of acid precursors (e.g. SO_2 and NO_x) have occurred during rapid industrialization and urbanization in China (Lu et al., 2011; Liu et al., 2013; Mao et al., 2014). Simultaneously, ammonia (NH_3) emission has also increased rapidly (Liu et al., 2013), neutralizing sulfuric and nitric acids in rainwater and subsequently generating significant acidification when deposited (as NH_4^+) to the soil surface (Galloway, 1995). Widespread areas in China, especially the southern regions, have been receiving high levels of acid rain (Larssen et al., 2006; Du et al., 2015), which has contributed to several key environmental issues, including acidification of soils and waters (Duan et al., 2016; Zhu et al., 2016), leaf injury and forest decline (Yu et al., 1990; Fan and Wang, 2000), loss of biodiversity (Liu et al., 2011), and damage of calcareous (e.g. concrete and marble) buildings and metal materials (Maeda et al., 2001).

Acid rain indirectly affects plant growth by inducing the leaching of soil nutrient cations and/or increasing the availability of toxic metals, especially aluminum, or directly by damaging the foliage (Haines and Carlson, 1989; Shriner et al., 1990; Singh and Agrawal, 2007; De Vries et al., 2015). The more acute direct injury of acid rain to plant foliage includes physiological (e.g. reduction in photosynthetic rate, variation in stomatal conductance and decrease in chlorophyll content) and morphological alternations (e.g. decrease in thickness of cuticle, reduction in leaf area, discoloration and occurrence of necrotic spots) (Baker and Hunt, 1986; Fan and Wang, 2000; Singh and Agrawal, 2007; Matsumura and Izuta, 2017a; Kohno, 2017). Although efforts have been made to improve the assessment of the indirect soil mediated ecological effects of acid rain in China (e.g. Larssen et al., 2006; Liu et al., 2011; Duan et al., 2016), a systematic assessment of direct foliage injury by acid rain across terrestrial plants is still lacking. Based on preference of soil acidity, terrestrial plants are usually categorized into calcicole (preferring lime-rich soils), ubiquist (preferring neutral soils) and calcifuge (preferring acidic soils) species (Lee, 1998). However, the linkage between the root preference of soil acidity and the direct foliage injury by acid rain remains unclear.

Based on recent reviews of acid rain exposure experiments on Asian trees, crops and garden plants, Matsumura and Izuta (2017a) and Kohno (2017) concluded that visible leaf injury indicators, such as necrotic spots, defoliation and discoloration, are not affected by acid rain up to a level of pH 4.0, being a level that is hardly exceeded in Asia. However, acid rain exposure experiments have also indicated more subtle direct leaf injury effects of acid rain, including a reduction of leaf chlorophyll content (Baker and Hunt, 1986; Fan and Wang, 2000; Singh and Agrawal, 2007; Matsumura and Izuta, 2017a; Kohno, 2017), that may affect plant growth. Leaf chlorophyll is essential in photosynthesis to support plant growth and is a sensitive indicator of the damaging effect of various environmental stresses on leaf function and health (e.g. Knudson et al., 1977; Carter and Knapp, 2001; Adams and Demmig-Adams, 2004). Leaf chlorophyll content is also highly correlated with gross primary production and net primary production estimates over the globe (Frankenberg et al., 2011). Surface characteristics are important in determining the leaf water holding capacity, foliar permeability and penetration, and rates of exchange of water and dissolved substances between plant and atmosphere (Fernández and Eichert, 2009). Therefore, leaf surface characteristics can affect the sensitivity to foliar injury, including the impact of leaf chlorophyll content as an indicator of it, by acid rain (Haines et al., 1985; Sant'Anna-Santos et al., 2006; Singh and Agrawal, 2007). For instance, plant species with a thinner cuticle and higher leaf water holding capacity are found to be more susceptible to leaf damage from simulated acid rain (Haines et al., 1985). Therefore, the direct leaf damage by acid rain may vary across functional groups due to variations in leaf surface characteristics. Considering the difference in leaf traits, we hypothesized that leaf chlorophyll content of deciduous broadleaf species is more susceptible to acid rain than evergreen species, in view of the thicker cuticle and lower leaf water holding capacity of evergreen species.

Many plants are economically cultivated to provide food (e.g. cereal, vegetable and fruit) and timber or are grown for ornamental purposes in gardens and urban greening projects. A recent analysis indicates the occurrence of urban acid islands in southern China, implying a higher risk of acid rain to reduce the growth and productivity of forest trees and crop plants in suburbs and urban areas (Du et al., 2015). Therefore, it is also of essential importance to assess the plant sensitivity to acid rain across economic use types, as the findings will then have useful implications to guide a regional planting plan to avoid potential economic loss.

In this study, we synthesized data from published literature on experiments of simulated acid rain in China to assess the direct effects of acid rain on leaf chlorophyll content of terrestrial plant species across soil acidity preference categories, functional groups and economic use types. Moreover, the implications for sustainable ecosystem management in the context of acid rain were also discussed.

2. Material and methods

2.1. Data set

We conducted a literature survey by using the keywords 'acid rain' and 'chlorophyll' in the online library of China National Knowledge Infrastructure (http://www.cnki.net/) and ISI Web of Science (http://isiknowledge.com). We collected data from reports and articles (published during 1985–2015) on experiments that simulate the direct effects of acid rain on leaf chlorophyll content of terrestrial plant species in China by exposing them to acid solutions with varying pH levels. The acid solution, a mixture of diluted sulfuric and nitric acids with pH ranging mainly from 2.0 to 5.6 (natural pH of precipitation, Galloway et al., 1984) and using treatment intervals of 0.5 or 1.0 pH unit (Table S1), was sprayed as a mist either on potted or field cultivated plants. When experimental data for one species were derived from two or more references (e.g. *Brassica napus, Carya cathayensis* and *Cinnamomum camphora*), the information was recorded separately (Table S1). The sum content of chlorophyll *a* and chlorophyll *b* was either assayed by an extraction-spectrophotometry method or directly measured by a chlorophyll meter (Table S1).

We recorded the species name, acid treatment (pH levels applied) and corresponding chlorophyll content directly from tables or digitized from figures using a GetData Graph Digitizer (Version 2.25, http://www.getdatagraph-digitizer.com). Our database consisted of experimental results for 67 terrestrial plant species, including 25 trees, 7 shrubs and 35 herbs (Table S1). For trees and shrubs, the experiments were generally conducted by using seedlings. Detailed information on the recorded species, acid solution, pH of acid rain treatment, duration of experiment, method of chlorophyll content measurement and site location (longitude and latitude), with the related reference is given in the supplementary information (Table S1).

2.2. Data analysis

In order to make the results from different measurement methods (either extraction-spectrophotometry or chlorophyll meter measurement) comparable, the value of leaf chlorophyll content for each species was standardized by being divided by that of the control treatment. If two or more experiments were conducted to one species, all data were pooled for further statistical analysis. A linear regression model was applied to explore the relationship between the standardized leaf chlorophyll content and the level of pH treatment according to Eq. (1),

$$Chl = k\mathrm{pH} + b, \quad (1)$$

where *Chl* is the standardized leaf chlorophyll content, pH is the pH level of the acid treatment, *k* and *b* are parameters. Because a lower

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