Environmental Pollution xxx (2017) 1–4

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Non-linear direct effects of acid rain on leaf photosynthetic rate of terrestrial plants☆

Dan Dong [a, b], Enzai Du [a, b, *], Zhengzhong Sun [a, b], Xuetong Zeng [a, b], Wim de Vries [c, d]

[a] State Key Laboratory of Earth Surface Processes and Resource Ecology, Beijing Normal University, Beijing, 100875, China
[b] Faculty of Geographical Science, Beijing Normal University, Beijing, 100875, China
[c] Wageningen University and Research, Environmental Research (Alterra), PO Box 47, 6700 AA Wageningen, The Netherlands
[d] Wageningen University and Research, Environmental Systems Analysis Group, PO Box 47, 6700 AA Wageningen, The Netherlands

ARTICLE INFO

Article history:
Received 20 June 2017
Received in revised form
1 September 2017
Accepted 5 September 2017
Available online xxx

Keywords:
Acid rain
Non-linear effect
Photosynthesis
Herbs
Woody plant

ABSTRACT

Anthropogenic emissions of acid precursors have enhanced global occurrence of acid rain, especially in East Asia. Acid rain directly suppresses leaf function by eroding surface waxes and cuticle and leaching base cations from mesophyll cells, while the simultaneous foliar uptake of nitrates in rainwater may directly benefit leaf photosynthesis and plant growth, suggesting a non-linear direct effect of acid rain. By synthesizing data from literature on acid rain exposure experiments, we assessed the direct effects of acid rain on leaf photosynthesis across 49 terrestrial plants in China. Our results show a non-linear direct effect of acid rain on leaf photosynthetic rate, including a neutral to positive effect above pH 5.0 and a negative effect below that pH level. The acid rain sensitivity of leaf photosynthesis showed no significant difference between herbs and woody species below pH 5.0, but the impacts above that pH level were strongly different, resulting in a significant increase in leaf photosynthetic rate of woody species and an insignificant effect on herbs. Our analysis also indicates a positive effect of the molar ratio of nitric versus sulfuric acid in the acid solution on leaf photosynthetic rate. These findings imply that rainwater acidity and the composition of acids both affect the response of leaf photosynthesis and therefore result in a non-linear direct effect.

1. Introduction

Anthropogenic emissions of acid precursors (especially SO_2 and NO_x) have enhanced global occurrence of acid rain, especially in East Asia (Vet et al., 2014). Previous studies have indicated that acid rain affects plant growth both indirectly by inducing nutrient leaching and increasing availability of toxic heavy metals (e.g. De Vries et al., 2015) and directly by damaging the foliage (e.g. Singh and Agrawal, 2007). The 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. reduction in thickness of cuticle and occurrence of necrotic spots) (Singh and Agrawal, 2007; Matsumura and Izuta, 2017; Kohno, 2017; Du et al., 2017). Leaf photosynthesis of terrestrial plants drives a large land carbon sink from the atmosphere, approximately offsetting 30% of the CO_2 emissions from anthropogenic activities (Le Quéré et al., 2015). Although research efforts have greatly improved our understanding of the indirect, soil mediated effects of acid rain on terrestrial ecosystems (Likens et al., 1996; Menz and Seip, 2004; Larssen et al., 2006; Singh and Agrawal, 2007; Duan et al., 2016), a systematic assessment of the direct effect on leaf photosynthesis is still lacking.

Acid rain directly suppresses leaf function by eroding surface waxes and cuticle (Haines et al., 1985; Percy and Baker, 1990) and leaching base cations (e.g. calcium, magnesium, and potassium) from mesophyll cells (DeHayes et al., 1999; Shigihara et al., 2008). However, foliar uptake of nitrates from acid rainwater, which is generally a solution mixture of nitric and sulfuric acids, may benefit leaf photosynthesis and plant growth (Sparks, 2009; Nair et al., 2016). These tradeoffs may lead to a non-linear direct effect of acid rain on leaf function, such as a possible increase in leaf photosynthesis at low acidity and a reduction at high acidity. Based on visible indicators such as necrotic spots and necrosis, earlier experiments indicate that simulated acid rain exposure induces

☆ This paper has been recommended for acceptance by Dr. Sarah Michele Harmon.

* Corresponding author. State Key Laboratory of Earth Surface Processes and Resource Ecology, Beijing Normal University, Beijing, 100875, China.
E-mail address: enzaidu@bnu.edu.cn (E. Du).

http://dx.doi.org/10.1016/j.envpol.2017.09.005
0269-7491/

direct foliar injuries below certain pH thresholds (Izuta, 1998). Unfortunately, these visible foliar indicators only reflect a direct injury by acid rain below a certain pH level, while the potential positive effect above a certain pH threshold cannot be identified with those indicators (Shan, 1998; Matsumura and Izuta, 2017; Kohno, 2017). More sensitive variables, such as leaf photosynthetic rate, are likely capable to track the hypothesized non-linear leaf responses to acid rain across multiple pH levels.

Widespread areas in China, especially the southern regions, have been exposed to acid rain with low pH levels, while inversely other regions are characterized by near neutral pH values (Larssen et al., 2006; Du et al., 2015). Despite of the fact that there has been emerging experimental research in China by directly applying acid solutions to plant leaves (see Table S1), the direct effects of acid rain on leaf photosynthetic rate have not yet been systematically evaluated. Here we synthesized data from the published literature on manipulated acid rain experiments with a mixture of diluted sulfuric and nitric acids in China to test the hypothesis of a non-linear effect of acid rain on leaf photosynthetic rate.

2. Material and methods

By conducting a survey of the online library of China National Knowledge Infrastructure (http://www.cnki.net/) and ISI Web of Science (http://isiknowledge.com), we collected data from published literature (peer-reviewed journal papers and dissertations) on experiments that simulate the direct effects of acid rain on leaf photosynthetic rate of terrestrial plant species in China. The acid solution, a mixture of diluted sulfuric and nitric acids with pH ranging from 2.0 to 5.6 (the pH value of pure water in equilibrium with ambient atmospheric CO_2, Galloway et al., 1984) and using treatment intervals of 0.5 or 1.0 pH unit (Table S1), was directly sprayed on leaves of either potted or field cultivated plants. When experimental data for one species were derived from two or more references, the information was recorded separately. We recorded the species name, acid treatment (pH level) and corresponding photosynthetic rates, either directly from tables or digitized from figures. Measurements of photosynthetic rates were conducted by using portable photosynthesis systems (e.g., LI-6400, LICOR, USA; CIRAS-1, PP-System International Ltd, UK).

Our database consisted of experimental results for 49 terrestrial plant species, including 20 trees, 12 shrubs and 17 herbs. Detailed information on the recorded species, location of the site (longitude and latitude), acid solute (as indicated by molar ratio of nitric versus sulfuric acid), pH of acid rain treatment, treatment duration, frequency of treatment, method of photosynthetic rate measurement, and the related reference is given in the supplementary information (Table S1). The ratios of nitric versus sulfuric acid were generally based on locally observed ratios in rainwater and ranged from 0.13 to 0.77, reflecting the range observed in southern China (Du et al., 2015).

As photosynthetic rate was measured under varied conditions, we calculated the standardized impact of the acid treatment on photosynthetic rate by dividing the rate after the treatment by that of the control treatment, to make data comparable across species. Table S1 includes both the mean measured photosynthetic rate and the standardized mean photosynthetic rate, being the relative effect of the acid rain treatment. If two or more experiments were conducted for one species, data were averaged for further statistical analysis. The effects of rain acidity on standardized photosynthetic rate at species level were tested by using one-way ANOVA and the sensitivity of leaf photosynthetic rate to increasing rain acidity was evaluated based on the slope of linear regression analysis. We conducted a multivariate regression model to address the effects of rainwater pH, the role of the composition of the acid solution (nitric versus sulfuric acids), treatment duration and their interactions on standardized photosynthetic rate. All statistical analyses were performed using the R software (version 3.2.4; R Development Core Team; http://www.r-project.org/). Figures were created using Sigma Plot 10.0 for Windows (Systat Software, San Jose, CA, USA). Values were mean ± standard error, if not specially noted.

3. Results and discussion

Acid rain exerted significant effects on leaf photosynthesis over the pH range from 2.0 to 5.6 ($F_{7, 180} = 14.18$, $p < 0.001$; Fig. 1). In line with our hypothesis, acid rain showed a neutral to positive effect on leaf photosynthetic rate at low acidity (above pH 5.0) and a negative effect below that level (Fig. 2). Multivariate linear regression analysis indicate a significant negative effect of rainwater acidity (as indicated by a positive correlation with rainwater pH) ($p < 0.001$), a significant positive effect of the molar ratio of nitric versus sulfuric acid on standardized leaf photosynthetic rate ($p = 0.004$) and a significant negative interaction between rainwater acidity (positively correlated with rainwater pH) and the molar ratio of nitric versus sulfuric acid ($p = 0.03$) (Table 1), suggesting a trade-off effect of rain water acidity and the composition of the solute acids on leaf photosynthetic rate.

Specifically, leaf photosynthetic rate of woody species showed a significant increase in response to acid rain at pH 5.0 ($F_{1, 36} = 20.33$, $p < 0.001$), while the effect on herbs was insignificant ($F_{1, 21} = 0.49$, $p = 0.49$) (Fig. 2). In comparison to short-lived and fast-growing herbs, woody species generally have lower leaf nitrogen contents and are more constrained by nitrogen (Han et al., 2005; Ågren, 2008). Therefore, a foliar fertilization effect via direct leaf nitrogen uptake from the rainwater is more likely to promote leaf photosynthesis and override the negative effect in woody plants than in herbs (Shan, 1998; Sparks, 2009; Fernández and Eichert, 2009; Nair et al., 2016). The benefit of foliar nitrogen uptake is thus more limited for herb species and seems only be capable to compensate the negative effect of acidity, thus resulting in a neutral effect at pH 5.0.

When exposed to acid rain with an acidity below pH 5.0, leaf photosynthetic rate showed a significant reduction of 10.7% per pH unit for herbs ($p = 0.005$) and 11.6% per pH unit for woody species

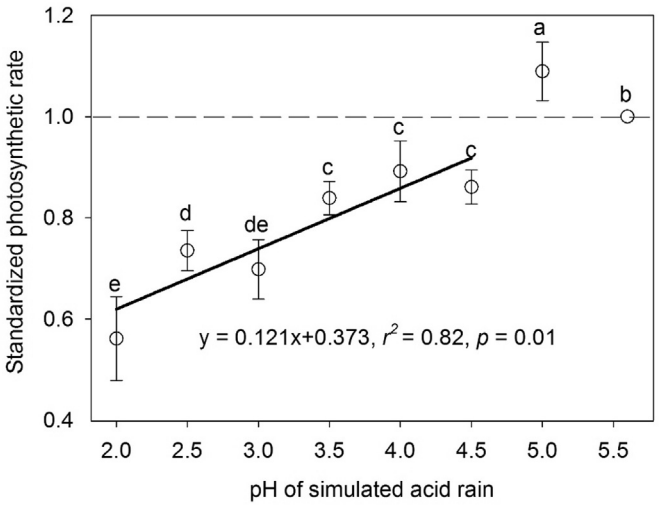

Fig. 1. Effects of simulated acid rain on standardized leaf photosynthetic rate of terrestrial plants in China. Same superscripted letters mean no significant difference and different letters mean a significant difference at $p < 0.05$. Values include the mean ± standard error.

Please cite this article in press as: Dong, D., et al., Non-linear direct effects of acid rain on leaf photosynthetic rate of terrestrial plants, Environmental Pollution (2017), http://dx.doi.org/10.1016/j.envpol.2017.09.005