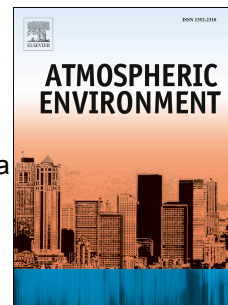


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# Seasonal variations of nitrate dual isotopes in wet deposition in a tropical city in China

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## Abstract

Monthly analytical results for more than two years long of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate in wet deposition are reported for a tropical city of Zhanjiang in the southernmost mainland China, in an effort to elucidate  $\text{NO}_x$  sources and its oxidation pathways to nitrate. The results showed that monthly variations of  $\delta^{18}\text{O}-\text{NO}_3^-$  responded well to changes in sunshine hours, with lower  $\delta^{18}\text{O}-\text{NO}_3^-$  values corresponding to longer sunshine hours. This pattern suggests that  $\text{NO}_x$  oxidation via the OH radical was the predominant pathway, which, by estimate, accounted for 87% in winter and 94% in summer, for nitrate formation. Remarkably, we found that the  $\delta^{18}\text{O}-\text{NO}_3^-$  here are prominently low relative to previous studies, likely due to that annual sunshine hours in this tropical city is relatively long. Moreover, available data of reported  $\delta^{18}\text{O}-\text{NO}_3^-$  in wet deposition showed an increasing trend with latitude, reflecting a shift of the predominant  $\text{NO}_x$  oxidation pathways from those via the OH radical in low latitudes to those via  $\text{O}_3$  in high latitudes, corresponding to the decrease of sunshine hours. A temporarily co-variation of  $\delta^{15}\text{N}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$  was observed, exhibiting higher values in dry winter and lower values in wet summer, which was attributed to the washout effect on the dual isotopes. During wet seasons, complete nitrate washout suggests that  $\delta^{15}\text{N}-\text{NO}_3^-$  in precipitation should be similar to the nitrate formed in the atmosphere, and thereby can be used for source apportionment. A Bayesian model showed that the source of atmospheric nitrate deposition is mainly natural (61%) in Zhanjiang, with less anthropogenic contribution.

**Keywords:** Dual nitrate isotopes; wet deposition;  $\text{NO}_x$  oxidation pathways; nitrogen source; tropical area

## 1. Introduction

Atmospheric deposition of nitrate ( $\text{NO}_3^-$ ) increased remarkably during the past decades due to

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