Online Supplemental Material

Impact of an accidental explosion in Tianjin Port on enhanced atmospheric nitrogen deposition over the Bohai Sea inferred from aerosol nitrate dual isotopes

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Text S1

In 2004, the technical transformation project of Sichuan Chemical Company Limited was faulty and severely exceeded sewage discharged for nearly 20 days; In 2005, the explosion occurred in the double-benzene plant of PetroChina Jilin Petrochemical Co., resulting in the influx of benzene and nitrobenzene, strong carcinogens, of about 100 tons into the river; In 2008, a mixture of approximately 300 kg of raw materials from the Shanghai Pesticide Plant leaked, resulting in a wide range of irritating gases in the downtown area; In 2011, a serious oil spill occurred in the Penglai 19-3 oilfield in the Bohai Sea, with a contaminated sediment area of 1600 km^2.

Text S2

Particulate matter was collected every 3 days on the quartz fiber filter (preheated

6h at 450°C) by a Tisch high volume sampler at a flow rate of 1.13 m^3 min^{-1}. The duration of every sampling was 24 h beginning at 06:00 am (LST). Synchronously, blank samples were collected to subtract possible contamination occurring in sampling processes. Before and after each sampling, the filters were all subjected to a 24 h equilibration at 25 ± 1°C and 50% ± 2% relative humidity, then analyzed gravimetrically using a Sartorius MC5 electronic microbalance (±10 μg sensitivity). Each sample was weighted at least three times, and acceptable difference among the repetitions was < 20 μg for sampled filters and 10 μg for blank filters. After weighting, filters were stored in refrigerators (−20°C) until chemical analysis.

Nitrous oxide (N_2O) conversion method was used to detect the $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- on BH Island (McIlvin and Altabet 2005). Briefly, NO_3^- solution was diluted to 15 μmol L^{-1} in a 5-mL solution with 0.5 mol L^{-1} NaCl. 0.3 g cadmium powder was then added into and the pH was adjusted to about 9 by the injection of 0.1 mL of imidazole (1 mol L^{-1}). After capped tightly, the processed samples were ultrasonically oscillated for 2h at 40°C for reducing the NO_3^- to NO_2^-. Here, the reduction rate was determined to be 98.33% ± 6.65%. Standing for 12 h, 4 mL of solution was further transferred to a new sample bottle and sodium azide (1:1 of 20% acetic acid and sodium azide, and purged with helium at 70 mL min^{-1} for 10 min) was injected for reaction. After 30 minutes, the reaction was stopped by 0.4 mL of NaOH (10 mol L^{-1}). The $\delta^{15}N$ and $\delta^{18}O$ of the N_2O produced were analyzed based on an isotope ratio mass spectrometer, and the $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values were reported in parts per thousand relative to standards (international reference materials: IAEA-NO_3^-, USGS32, USGS34, and USGS35):

$$\delta^{15}N = \left[\left({}^{15}N/{}^{14}N \right)_{sample} \Big/ \left({}^{15}N/{}^{14}N \right)_{standard} - 1 \right] \times 1000 \quad \text{(S1)}$$

$$\delta^{18}O = \left[\left({}^{18}O/{}^{16}O \right)_{sample} \Big/ \left({}^{18}O/{}^{16}O \right)_{standard} - 1 \right] \times 1000 \quad \text{(S2)}$$

Determined from the replicates, the analytical precision was less than 0.30‰ for $\delta^{15}N$-NO_3^- and 0.61‰ for $\delta^{18}O$-NO_3^-, respectively. It should be noted that NO_2^- concentrations were lower than the detection limit and less than 2% of the NO_3^-; therefore, they were ignored during the isotopic analyses.

Organic carbon (OC) and element carbon (EC) were analyzed by a Desert Research Institute (DRI) Model 2001 Carbon analyzer based on the Interagency Monitoring of Protected Visual Environment (IMPROVE_A) thermal/optical reflected (TOR) protocol. Detailed testing procedure was referred in our previous study (Zong et al. 2015). Regarding water-soluble ions including Na^+, K^+, Ca^{2+}, Mg^{2+}, NH^{4+}, Cl^-, NO_3^-, and SO_4^{2-}, one punch with 47 mm diameter was cut off, and then was subjected to Milli-Q water. Samples were ultrasonically extracted for 20 min, and the extracts were filtered. Ion concentrations were measured by the ion chromatograph with the detection limit of 10 ng ml^{-1} and an error < 5.2%. All ion concentrations were blank-corrected by subtracting the average field blank values (Wang et al. 2014).

Text S3

Monte Carlo methods can be used to solve any problem having a probabilistic interpretation. By the law of large numbers, integrals described by the expected value of some random variable can be approximated by taking the empirical mean (a.k.a. the sample mean) of independent samples of the variable. When the probability distribution of the variable is parametrized, mathematicians often use a Markov chain Monte Carlo (MCMC) sampler. The central idea is to design a judicious Markov chain model with a prescribed stationary probability distribution. That is, in the limit, the samples being generated by the MCMC method will be samples from the desired (target) distribution (Goulden et al. 1996).

$$C_5H_{12}+5NH_3 \xrightarrow[\text{electric arc}]{1450^\circ\text{C}} 5HCN+11H_2;\ HCN+NaOH \rightarrow NaCN+H_2O \tag{S3}$$

$$4NH_3+5O_2 \xrightarrow[\text{catalyst}]{\text{HT/HP}} 4NO+6H_2O;\ 2NO+H_2O+2O_2 \xrightarrow{\text{catalyst}} 2HNO_3$$
$$NH_3+HNO_3 \rightarrow NH_4NO_3 \tag{S4}$$

$$NH_4NO_3+KCl \xrightarrow[\text{cooling}]{\text{evaporation/filtration}} KNO_3+NH_4Cl \tag{S5}$$

$$N_2+3H_2 \xrightarrow[\text{catalyst}]{\text{HT/HP}} 2NH_3 \tag{S6}$$

$$NO+O_3 \rightarrow NO_2+O_2 \tag{S7}$$

$$NO_2 + hv \rightarrow NO + O \quad (S8)$$

$$O + O_2 \rightarrow O_3 \quad (S9)$$

$$NO_2 + OH \rightarrow HNO_3 \quad (S10)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (S11)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (S12)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (S13)$$

Reference

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