

稳定同位素用于闽南夏季云下洗脱过程的研究*

姚小红 崔平** 郝吉明

(清华大学环境工程系, 北京 100084)

摘要 使用稳定同位素方法对闽南夏季云下洗脱过程进行研究; 对闽南夏季降水中稳定同位素丰度比进行了测试. 氢氧同位素丰度比分析发现, 降水氢氧同位素丰度比存在较大分馏, 但同一降水云系中 $\delta D/\delta^{18}O$ 值是稳定的, 可以作为判别降水来源的特征量. 对降水中硫同位素丰度比分析发现, 当大气中气溶胶和气体硫同位素均呈负值时, 降水中富集 ^{34}S , 反之相反. 并使用稳定同位素平衡模型估算事件型降水云下洗脱过程的作用. 厦门前期降水云中、云下洗脱硫的比例分别为 19.5% 和 80.5%, 中期降水云中、云下洗脱硫的比例分别为 32.3% 和 57.7%, 后期降水云中、云下洗脱硫的比例分别为 53% 和 47%, 漳州云中、云下洗脱比例接近.

关键词 SO_2 , 云下洗脱, 稳定同位素, 平衡模式, 闽南, 夏季.

硫化物对酸雨的致酸作用发生在云中、云下洗脱 2 个过程中^[1,2]. 在我国, 大气中 SO_2 、气溶胶浓度较高, 云下洗脱硫化物占相当大的比例, 准确估算云下洗脱硫化物的比例对揭示区域酸雨形成机制及控制酸雨都有重要意义. 目前研究云中、云下洗脱硫化物的比例主要通过洗脱模式^[3,4], 但洗脱模式的计算结果存在一定的不确定性, 本研究尝试使用稳定同位素方法研究这一过程^[5,6], 取得一些新结果.

1 试验部分

1992-08-17—1992-09-07, 对闽南地区夏季 2 次热带风暴降水进行观测, 并同时测定了大气污染物的组成. 设立降水采样点分别为泉州市环境监测站、漳州环境监测站、厦门环境监测站、海洋三所, 采用 8 只聚乙烯桶分时段收集降水, 每 5L 水作为一个样品, 现场测 pH, 过滤, 保存在冰箱中, 运回后, 取 50ml 用离子色谱测离子浓度, 其余样品在 80℃ 下蒸发至 100ml, 加入 10% $BaCl_2$ 溶液 10ml, 再加入 1mol/L HCl 10ml 沉淀, 用 0.45 μm 的微孔滤膜过滤, $BaSO_4$ 沉淀在 100℃ 条件烘干, 在 900℃ 马沸炉中烘 2h 去杂质后, 用加热法测定其硫同位素丰度^[7,8].

2 稳定同位素平衡模式

大气中硫稳定同位素丰度用 $\delta^{34}S$ 表示:

$$\delta^{34}S(\text{‰}) = (R_{\text{样品}} - R_{\text{标准}}) / R_{\text{标准}} \times 1000 \quad (1)$$

考虑大气中 SO_2 氧化主要为均相和非均相过程, 云中和云下洗脱的硫化物主要包括 SO_2 和气溶胶中硫酸盐, 则可以有以下方程:

$$(^{32}K_{\text{hom}} + ^{32}K_{\text{het}}) [^{32}SO_2] = ^{32}K_{\text{aero}} [^{32}SO_4] \quad (2)$$

$$(^{34}K_{\text{hom}} + ^{34}K_{\text{het}}) [^{34}SO_2] = ^{34}K_{\text{aero}} [^{34}SO_4] \quad (3)$$

(2) 和 (3) 式中, K_{hom} , K_{het} 分别为大气中 SO_2 均相和非均相反应速度, K_{aero} 和 (4) 的 $K_{\text{in-cloud}}$ 为洗脱速率, 其中 $^{32}K_{\text{aero}} = ^{34}K_{\text{aero}}$, $[SO_4]$ 、 $[SO_2]$ 为质量浓度.

假设在降水短时间尺度内, 大气中气溶胶和 SO_2 处于稳态, 则有以下方程:

$$^{32}F_{\text{precip}} = ^{32}K_{\text{aero}} [^{32}SO_4] + ^{32}K_{\text{in-cloud}} [^{32}SO_2] \quad (4)$$

$$^{34}F_{\text{precip}} = ^{34}K_{\text{aero}} [^{34}SO_4] + ^{34}K_{\text{in-cloud}} [^{34}SO_2] \quad (5)$$

$A = ^{32}K_{\text{hom}} / ^{32}K_{\text{het}}$
式中, $^{32}F_{\text{precip}}$ 为 ^{32}S 的沉降速率, $^{34}F_{\text{precip}}$ 为 ^{34}S 的沉降速率.

$$\Delta^{34}S_{\text{a-g}} = (1 + \delta^{34}S_{\text{g}}/1000) \cdot \left(\frac{\alpha_{\text{hom}} + \alpha_{\text{het}} \times A}{1 + A} - 1 \right) \quad (6)$$

式中, α_{hom} 为均相分馏比, $\alpha_{\text{hom}} = 0.991(25^\circ)$, α_{het} 为非均相分馏比, $\alpha_{\text{het}} = 1.0165(25^\circ)$, $\Delta^{34}S_{\text{a-g}}$ 为气溶胶和 SO_2 同位素丰度差.

* 国家“八五”科技攻关课题(编号: 85-912-02-02)

** 现在中国环境科学研究院工作

收稿日期: 1997-05-20

$$\Delta^{34}\text{S}_{\text{w-g}} = (1 + \delta^{34}\text{S}_{\text{g}}/1000) \cdot (D - 1) \times 1000(\text{‰}) \quad (7)$$

$$D = \frac{{}^{32}K_{\text{hom}}\alpha_{\text{hom}} + {}^{32}K_{\text{het}}\alpha_{\text{het}} + {}^{32}K_{\text{in-cloud}}\alpha_{\text{in-cloud}}}{{}^{32}K_{\text{hom}} + {}^{32}K_{\text{het}} + {}^{32}K_{\text{in-cloud}}} \quad (8)$$

式中, $\Delta^{34}\text{S}_{\text{w-g}}$ 是降水和 SO_2 同位素丰度差, 考虑 SO_2 潮湿气溶胶表面反应机理与 SO_2 气液非均相反应机理一致, 仅仅因含水量的差异产生的 SO_2 反应速率的不同, 因此有 $\alpha_{\text{in-cloud}} = \alpha_{\text{het}}$, 引入参数:

$$S_{\text{in-cloud}} = \frac{{}^{32}K_{\text{in-cloud}}[\text{SO}_2] \times 100}{{}^{32}K_{\text{aero}}[\text{SO}_4] + {}^{32}K_{\text{in-cloud}}[\text{SO}_2]} \quad (9)$$

式中, $S_{\text{in-cloud}}$ 是云中洗脱比例, 将 (2) 式代入 (9) 式, 得到:

$$S_{\text{in-cloud}} = \frac{{}^{32}K_{\text{in-cloud}} \times 100}{{}^{32}K_{\text{hom}} + {}^{32}K_{\text{het}} + {}^{32}K_{\text{in-cloud}}} \quad (10)$$

将 A 和 B 代入 (10) 式得:

$$B = {}^{32}K_{\text{in-cloud}} / {}^{32}K_{\text{het}};$$

$$S_{\text{in-cloud}} = \left(\frac{AB}{1 + A + AB} \right) \times 100\% \quad (11)$$

B 可以从 (12) 式中求出:

$$B = \frac{(\alpha_{\text{het}} - Q)}{(Q - \alpha_{\text{het}})A} - 1 \quad (12)$$

Q 可以由 (13) 式求出:

$$Q = \frac{\Delta^{34}\text{S}_{\text{w-g}}}{(1 + \delta^{34}\text{S}_{\text{g}}/1000) \times 1000} + 1 \quad (13)$$

a 为海盐源的贡献率

$$a = [\text{Na}^+]_{\text{观测}} / [\text{SO}_4^{2-}]_{\text{观测}} \times 6.1 \times 100\% \quad (14)$$

3 结果与分析

收集 1992-08-17—09-07 2 次降水样品, 分析其同位素组成见表 1。从表 1 可以看出闽南地区降水中硫同位素丰度存在区域分异, 厦门环境监测站降水样品中硫同位素富集 ^{32}S , 其余各点降水样品硫同位素富集 ^{34}S , 随降水持续, 厦门环监站降水硫同位素呈富集 ^{34}S 趋势, (08-18—08-19 的水样中的降水有间断), 海洋三所降水受海洋影响显著, 因此降水中 ^{34}S 丰度为正值。从时间序列上看, 随降水持续, 降水中富集 ^{32}S (海盐硫酸根 ^{34}S 为 + 20.0‰)。

表 1 闽南地区夏季降水稳定同位素丰度¹⁾/‰

地点	时段	8-18	15:30—16:00	$\delta^{34}\text{S}$	δD	$\delta^{18}\text{O}$
厦门	08-18	16:30—19:00		-1.8	-36.1	-5.86
厦门	08-18	19:00—23:00		2.1	-35.3	-5.73
厦门	08-18	19:00—23:00		3.6	-43.6	-7.02
厦门	08-18	23:00—19日9:00		-1.2	-46.3	-7.02
厦门	08-20	8:00—9:00		-7.1	-29.8	-4.31
海洋三所	08-18	15:30—16:00		12.4	-33.4	-4.94
海洋三所	08-18	16:00—19:00		10.1	-34.6	-5.54
海洋三所	08-18	19:00—23:00		10.4	-34.9	-5.85
海洋三所	08-18	23:00—19日9:00		5.8	-38.4	-5.92
海洋三所	08-20	8:00—9:00		9.4	-47.0	-7.13
泉州	08-17—08-18			5.0	-34.5	-5.2
泉州	08-31—09-01			-22.4	-97.2	-13.07
泉州	09-06			-0.1	-26.9	-3.87
漳州	08-17—08-18			9.1	-39.9	-6.12
漳州	09-06			17.5	-57.9	-8.93
漳州	08-31—09-01			17.1	-52.5	-6.36

1) D 为降水中氘同位素丰度, $\delta^{18}\text{O}$ 为降水中 ^{18}O 同位素丰度

从氢氧同位素丰度比分析, 由于氢同位素质量小, 其同位素质量比较大, 因此在降水形成过程有较大的同位素分馏, 这是识别降水来源的特征量。从表 1 可以看出, 有同一来源的 08-18 降水 δD 值比较接近, 而不同来源的降水 δD 值有较大波动。从 $\delta\text{D}/\delta^{18}\text{O}$ 之比分析, 08-18 闽南 4 个监测点比值均为 6.5, 而其余观测数据比值在 7.0 左右, 进一步说明 08-18 闽南降水属同一降水云系。08-31 泉州降水中 δD 和 $\delta^{18}\text{O}$ 与其余各点各时段有显著性差异, δD 和 $\delta^{18}\text{O}$ 比值为 7.5, 这表明此场降水来源与其余降水样品有差异, 这可能是降水中 $\delta^{34}\text{S}$ 异常的一重要原因。

降水中 Na^+ 和 SO_4^{2-} 比取平均值为 0.494, 由此计算出海盐的贡献 $a = 8.1\%$ 。测得厦门站大气中 SO_2 的同位素丰度为 -4.8‰, 测得大气气溶胶中硫同位素丰度如表 2 所示。

表 2 闽南地区气溶胶中硫稳定同位素丰度/‰

粒径/ μm	7	7—2.0	2.0
漳州	6.0	9.1	11.0
泉州	-9.1	-0.4	
厦门环监站	-1.4	-2.8	-5.8
厦门海洋三所	14.6		

将表 2 中的参数代入方程 (9) 至 (14) 中, 得到结论如表 3 所示。

表3 厦门站降水中硫化物来源/ %

洗脱阶段	云中	云下
前期降水	19.5	80.5
中期降水	32.3	57.7
后期降水	53	47

比较计算结果与文献值, 厦门地区云中洗脱硫化物的比例较大, 尤其是在后期降水中. 可能的原因是, 厦门地区夏季存在高空酸化带, 云下大气污染物浓度小所致.

采用大气采样器收集 09-02—06 漳州大气中 SO_2 样品, 分析其硫稳定同位素丰度值为 6.5, 将 SO_2 硫同位素数据及气溶胶和降水硫同位素数据代入以上方程组, 可得结论, 如表 4 所示.

表4 漳州地区夏季降水中硫的来源/ %

监测日期/月-日	云中洗脱	云下洗脱
09-06	58.3	41.7
08-31—09-01	48.8	51.2

从表 4 中可以看出, 漳州地区 09-06、08-31—09-01 的 2 次累积降水样品中硫化物来自云中、云下洗脱过程的比例和厦门站后期降水中硫化物来自云中、云下洗脱过程的比例接近. 就区域总硫沉降而言, 云中洗脱硫化物比例略大于云下洗脱, 这一结果进一步说明闽南地区夏季云中洗脱硫化物是降水中硫化物重要来源. 这是闽南地区近地面层大气中 SO_2 、 NO_x 等致酸前体物浓度低, 但降水已酸化, 部分降水 $\text{pH} < 4.6$ 的重要原因之一.

4 小结

闽南地区夏季降水中氢氧同位素存在较大

分馏, 但同一降水云系中, $\delta\text{D}/\delta^{18}\text{O}$ 值较稳定, 可以作为判别降水来源的特征量.

当大气中气溶胶和气体硫同位素均呈负值时, 随降水持续, 降水中富集 ^{34}S , 反之相反.

稳定同位素模型估算事件型降水云下洗脱过程结果表明, 厦门前期降水云中、云下洗脱硫的比例分别为 19.5%、80.5%, 中期降水云中、云下洗脱硫的比例分别为 32.3%、57.7%, 后期降水云中、云下洗脱硫的比例分别为 53%、47%, 漳州云中、云下洗脱比例接近.

参 考 文 献

- 1 王文兴. 华南地区酸沉降源解析. 环境科学学报, 1992, **12** (1): 1—4
- 2 Lin X et al. Model simulation of rainout and washout from a warm stratiform cloud. Journal of Atmospheric Chemistry, 1990, **10**: 1—26
- 3 Jensen P K et al. General chemical reaction simulation applied to below-cloud scavenging. Atmospheric Environment, 1995, **29**(14): 1619—1625
- 4 Nriagu J O et al. Biogenic sulfur and the acidity of rainfall in remote areas of Canada. Science, 1987, **237**: 1189—1190
- 5 Wadleigh M A et al. Sulphur isotope tests of seasalt correction factors in precipitation. Water, Air and Soil Pollution, 1994, **77**: 1—16
- 6 Calhoun J et al. Sulfur isotope measurements of submicrometer sulphate aerosol particles over the Pacific Ocean. Geophysical Research Letters, 1991, **18**: 1877
- 7 Herut B et al. Sources of sulfur in rainwater as indicated by isotopic data and chemical composition Israel. Atmospheric Environment, 1995, **29**(7): 851—857
- 8 Mearns N C et al. Isotopes and atmospheric sulphur. Atmospheric Environment, 1995, **29**(18): 2553—2556
- 4 Conningham P T, Johnson S A and Yang R T. Variations in Chemistry of Airborne Particulate Material with Particle Size and Time Environ. Sci. Technol., 1974, **8**(2): 131
- 5 Kellner R and Maliss H. Fourier Transform Infrared Microscopy—A Tool for Speciation of Impactor Sampled Single Particles or Particle Clusters. Aerosol Sci. and Technol., 1989, **10**: 397
- 6 吴谨光主编. 红外光谱法在无机和配位化学基础研究中的应用. 近代傅利叶变换红外光谱技术及应用(下卷). 第 1 版. 北京: 科学技术文献出版社, 1994: 263

(上接第 12 页)

参 考 文 献

- 1 Koutrakis et al. An Improved Method for Measuring Aerosol Strong Acidity. Atmos. Environ., 1988, **22**: 157
- 2 Koutrakis et al. Equilibrium Size of Atmospheric Aerosol Sulfates as a Function of the Relative Humidity. Journal of Geophysical Research, 1989, **94**(D5): 6442
- 3 Conningham P T, Johnson S A. Spectroscopic Observation of Acid Sulfate in Atmospheric Particulate Samples. Science, 1976, **191**: 77

Dry Deposition Model for Sulfur Pollutants.

Gao Huiwang et al. (Institute of Physical Oceanography, Ocean Univ. of Qingdao, 266003): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 1—4

A dry deposition model for sulfur pollutants is developed, in which the effects of atmospheric conditions and surface types on the dry deposition velocity are considered. The dry deposition velocities of SO₂ and SO₄²⁻ are calculated over several typical land categories. The dry deposition velocities of SO₂ and SO₄²⁻ vary from 0.2—1.0cm/s and 0.1—0.8cm/s respectively. This dry deposition model is one of the bases of the study of Sulfur Deposition Model.

Keywords: sulfur pollutant, dry deposition velocity, numerical model, atmospheric.

Calculation of Critical Loads for Acid Deposition with the Simple Mass Balance Method.

Xie Shaodong, Hao, Jiming et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 5—8

Based on criteria of plant response, soil stability, aluminum concentration, alkalinity and pH, critical loads of acid deposition for all kinds of red earth in Liuzhou area were calculated by using the simple mass balance method. The results indicate the following: sandy red earth, red sandy soil, fluvo-aquic sandy soil, middle-erosion red earth and fluvo-aquic sandy red earth have lower critical load values of acid deposition, cinnamon red earth and infant red earth have higher values; in order to protect 95% of the Liuzhou soil area from effects of acid deposition, critical loads of acidity, potential acidity, sulfur deposition and nitrogen deposition for red earth are 1.8 keq·hm⁻²·a⁻¹, 1.9 keq·hm⁻²·a⁻¹, 0.70 keq·hm⁻²·a⁻¹ and 1.5 keq·hm⁻²·a⁻¹ respectively; critical load of acidity for surface water is 0.80 keq·hm⁻²·a⁻¹.

Keywords: acid deposition, critical load, red earth, simple mass balance method, Liuzhou Area.

Fourier Transform Infrared Transmission Spectroscopic Analysis of Bisulfate in Ambient Aerosols.

Liang Yongmei, Wan Meirong et al. (State Key Lab of Environ. Simulation and Pollution Control, Peking University, Beijing 100871), *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 9—12

This paper described the difference about IR absorption between sulfate and bisulfate, and chose the 750—500cm⁻¹ as quantitative analysis range for sulfate and bisulfate. Sulfate and bisulfate in aerosol samples which collected from Zhong Guancun, Beijing in 1994—1995, prepared by pressing into KBr pellets, were analyzed using fourier transform infrared (FTIR) transmission spectroscopy. Analysis results is 2.56—60.4 μg·m⁻³ and ND—5.7 μg·m⁻³ in terms of sulfate and bisulfate, respectively. The method presented in this paper offers a direct quantitative analysis for bisulfate.

Keywords: aerosols, bisulfate, FTIR quantitative analysis, Zhong Guancun Region, atmospheric determination.

Use of Stable Isotope for Evaluating Washout Process in Summer at Mingnan Area.

Yao Xiaohong et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 13—15

The stable isotope was used for evaluating washout process in summer at Mingnan Area. Abundance ratio of stable isotope of rainwater was determined in summer at Mingnan. It was found that there was a large isotope fraction in rainwater, but the value of δD/δ¹⁸O was stable within common cloud, and which could be used as characteristic variation to distinguish source of rainwater. According to analysis of sulfur isotope, if ratios of sulfur isotope were negative in both aerosol and SO₂, it would be abundant ³⁴S in rainwater. A stable isotope model was used to study washout process, the result showed that ratios of rainout and washout sulfur in beginning are 19.5%, 80.5% respectively, then the ratio become 32.3%, 57.7%, the ratio are 53%, 47% in the end. The ratios of two processes were almost equal in

Zhangzhou.

Keywords: SO₂, washout, stable isotope, model, Mingnan Area, summer.

Study of Organic Hydroperoxides and H₂O₂ Yields in Isoprene and O₃ Reactions.

Li Shuang et al. (The State Key Lab of Environ. Simulation and Pollution Control, Center of Environ. Sci., Peking Univ., Beijing 100871): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 16—18

The atmospheric reaction of isoprene with O₃ was simulated under the dark and room temperature in the 28.5L quartz reactor coupled with a Long Path Fourier Transform Infrared Spectrometer, while the Dual Channel H₂O₂ Analytical System was used to determine the production of organic hydroperoxides and H₂O₂. Yields measured respectively in the three repeated experiments are 3.8%, 4.3% and 3.9% for organic hydroperoxides with the average of 4.0%, and 2.2%, 1.6% and 1.8% for H₂O₂ with the average of 1.9%. The formation mechanisms of organic hydroperoxides and H₂O₂ were briefly discussed.

Keywords: isoprene, O₃, Dual Channel H₂O₂ Analytical System, organic hydroperoxides, H₂O₂.

The Atmospheric Diffusion Parameter in Various Terrain in Comparison with Each Other in Shandong Province.

Mao Hengqing (National Meteorological Center, Beijing 100081) *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 19—22

Analysing the experimental result in Shandong province, it is found that the atmospheric diffusion parameters vary obviously with terrain. The diffusion parameters are about as big as that of national standard in the plain and half to one class bigger than it in the mountain areas. In industrial park the cross-wind diffusion parameter is about the same as while the vertical one is one more class bigger than that of national standard. In coastal areas the cross-wind parameter is bigger slightly and the vertical one is smaller slightly than that of national standard. The pollutant diffusion density and the air diffusio-phoretic velocity are related directly to the diffusion parameter.

Keywords: atmospheric diffusion parameter, national standard, air pollutant, cross-wind

diffusion parameter, vertical diffusion parameter.

Cross-flow Membrane Bioreactor for Domestic Wastewater Treatment and Its Biological Behavior.

Xing Chuanhong, Qian Yi (State Key Lab of Environ. Simulation and Pollution Control, Dept. of Environ. Eng., Tsinghua Univ., Beijing, 100084), *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 23—26

It is proven that Crossflow Membrane BioReactor (CMBR) applied to domestic wastewater treatment, under conditions of hydraulic retention time 5h, sludge retention time 15d, membrane surface velocity 4m/s and membrane flux 75, 150L/(m²·h), is technically feasible and reliable during six weeks. Removal rate of COD, NH₃-N, and turbidity of the system are equal to or higher than 97%, 97% and 98%, SS and E. coli., 100%. The effluent quality is always better than the quality standard for reuse issued by the Ministry of Construction in China. An important formula to calculate the sludge concentration for CMBR at steady state is successfully derived from material balance equations. The apparent yield factor Y_g is approximately 0.65mgVSS/mg COD and the decay constant, 0.1d⁻¹. Furthermore, the bio-facies analysis of CMBR is included.

Keywords: crossflow, membrane, bioreactor, biological behavior, domestic wastewater.

Photochemical Treatment of Selected Organic Wastewater.

Zhu Chunmei et al. (State Key Lab. of Pollution Control and Resource Reuse, Dept. of Environ. Sci. and Eng., Nanjing Univ. 210093): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 27—30

The photochemical oxidation treatment for selected organic wastewaters which were hard to degrade and were performed by adding H₂O₂ or some semiconductor powder and bubbling of O₂ or O₃ under sunlight or a middle pressure mercury lamp. The results showed that the removal rates of COD, oil and volatile phenols were 26.4%—60%, 39.8%—97.8% and 86.3%—100% respectively for the wastewaters of oil refinery and coking industry; the removal rates of COD and decoloration rates were 48%—75%, 80%—100% for selected