



Using a dual isotopic approach to trace sources and mixing of sulphate in Changjiang Estuary, China

Si-Liang Li^{a,*}, Cong-Qiang Liu^a, Sivaji Patra^a, Fushun Wang^b, Baoli Wang^a, Fujun Yue^a

^aThe State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

^bInstitute of Applied Radiation, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 201800, China

ARTICLE INFO

Article history:

Available online 26 March 2011

ABSTRACT

The dual isotopic compositions of dissolved SO_4^{2-} in aquatic systems are commonly used to ascertain SO_4^{2-} sources and possible biogeochemical processes. In this study, the physical parameters, major anions and isotopic compositions of SO_4^{2-} in water samples from Changjiang River (Nanjin) to the East Sea in Changjiang Estuary were determined. The salinity ranged from 0‰ to 32.3‰ in the estuary water samples. The Cl^- , SO_4^{2-} concentrations and $\delta^{18}\text{O}\text{-H}_2\text{O}$ values followed the salinity variations from freshwater to seawater, which indicated that mixing processes might be a major factor involved in the distribution of water and solutes. The contents and isotopic compositions of SO_4^{2-} suggested that atmospheric deposition, evaporite dissolution and sulphide oxidation were the major sources of dissolved SO_4^{2-} in the freshwater of Changjiang River. In addition, the mixing model calculated by contents and isotopic compositions of SO_4^{2-} indicated that the mixing of freshwater and sea water was the major factor involved in SO_4^{2-} distribution in Changjiang Estuary. However, slightly elevated $\delta^{18}\text{O}\text{-SO}_4$ values were observed in the turbidity maximum zone, which suggested that biological processes might affect the O isotopic compositions of SO_4^{2-} there.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Sulphur is an important biological element that is also a major element of seawater and marine sediments. Sulphur has four main oxidation states and acts as an electron acceptor and electron donor for biogeochemical processes in redox reactions (Clark and Fritz, 1997). Isotopic compositions ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) can be useful indicators of SO_4^{2-} sources and biogeochemical processes in aquatic environments (Clark and Fritz, 1997; Mayer, 2005). Accordingly, several studies have employed the dual isotopic technique to identify the sources of SO_4^{2-} and transformation in rivers (Pawellek et al., 2002; Brenot et al., 2007; Calmels et al., 2007; Otero et al., 2008; Rock and Mayer, 2009). These studies have shown various degrees of success for distinguishing the sources and fate of SO_4^{2-} . However, few studies have used the dual isotopic method to explore SO_4^{2-} biogeochemistry in estuaries.

Estuaries play a key role in the water and solute transportation from rivers to the coastal sea. The Changjiang River is the largest river in China and transfers a large amount of freshwater into the East China Sea. A strong hydrologic regime occurring along the water bodies ultimately re-suspends bottom sediments in response to high tidal intrusions (Shen et al., 1992). The turbidity maximum zone is an important area for the mixing of freshwater

and sea water. Zhu et al. (2003) reported that the characteristics of phytoplankton in a high red tide occurrence area were related to freshwater entering the Changjiang River estuary. Additionally, organic matter preserved in the sediments was found to be predominantly controlled by the particulate organic matter based on stable isotopic analysis of the Changjiang Estuary (Zhou et al., 2006).

In this study, surface water and water column (16, 18, 19) samples were collected from downstream of Nanjin City to the East China Sea during June 2005 (Fig. 1). The dual isotopic composition of SO_4^{2-} combined with water and chemical data were used to ascertain the factors controlling SO_4^{2-} behavior, such as conservative mixing or possible biogeochemical processes, especially in the turbidity maximum zone.

2. Results and discussion

2.1. The variations of parameters and isotopic characteristics of water in Changjiang Estuary

The temperature of the water samples ranged from 20.2 °C to 28.7 °C, with a mean value of 24.3 °C. The pH of the water samples ranged from 7.0 to 8.7, with a median value of 7.9. Fresh water had lower pH values than the high salinity waters. The salinity increased from 0‰ to 32.3‰ from the Changjiang River to the East China Sea (Fig. 2). The Cl^- concentrations increased from

* Corresponding author. Tel.: +86 851 5890450; fax: +86 851 5891609.

E-mail address: lisiliang@vip.skleg.cn (S.-L. Li).

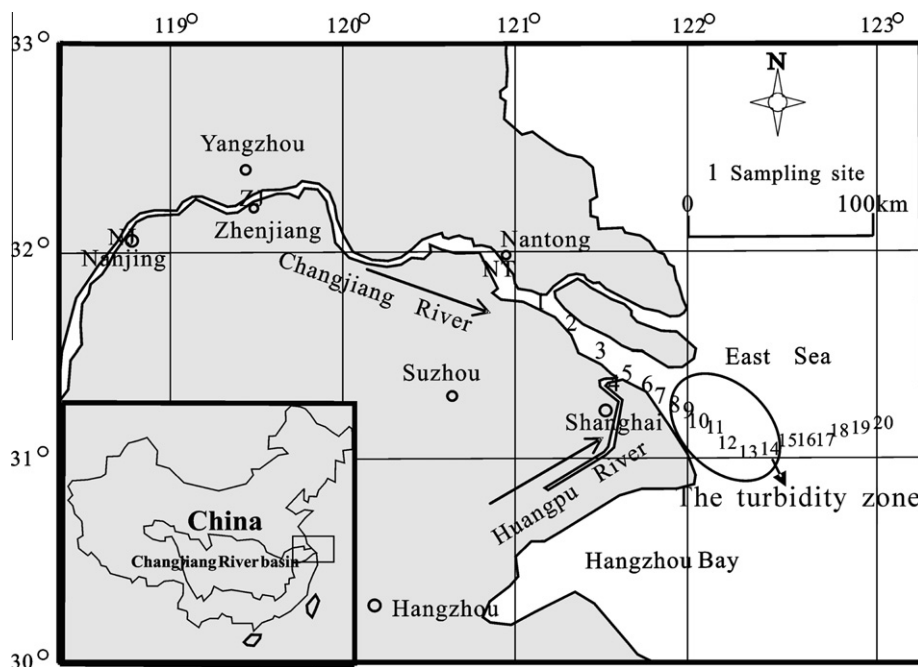


Fig. 1. Map showing the locations of sampling sites along the Changjiang Estuary.

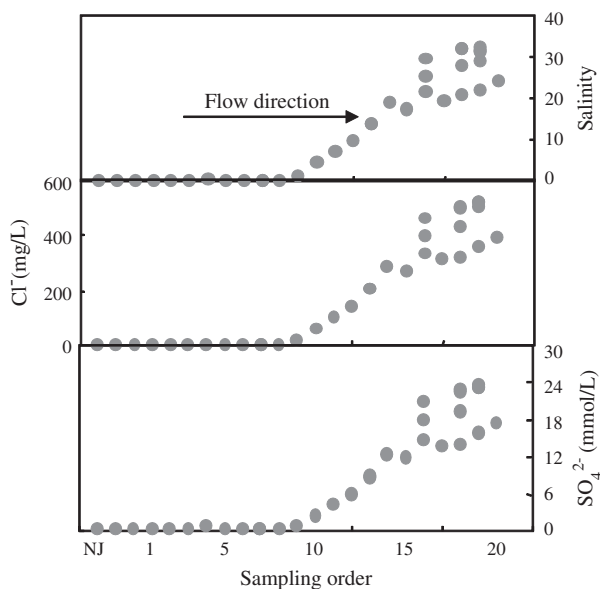


Fig. 2. Variations of salinity (‰) and major anions in waters from Nanjing to East Sea in the Changjiang Estuary.

0.12 mmol/L in freshwater to 517 mmol/L in high salinity waters. There was a good positive relationship between the salinity and Cl^- in the water (not shown). The vertical variations in the parameters in the water column are as follows: surface water had lower salinity and Cl^- concentrations than samples collected from deeper portions of the water column. The inhomogeneity of the water chemistry suggested that mixing between the fresh water and sea water was a slow process due to the complicated and large movement of water in the Changjiang Estuary. The SO_4^{2-} concentrations showed a similar trend to the salinity and Cl^- (Fig. 2), with values ranging from 0.14 mmol/L to 23.5 mmol/L being observed.

The spatial variations in the $\delta^{18}\text{O}$ values of the water were similar to the variations in salinity and Cl^- . The O isotope of water can

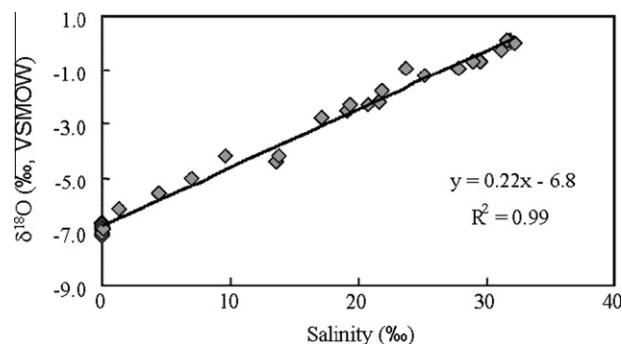


Fig. 3. Comparison between salinity and $\delta^{18}\text{O}$ -waters showing water mixing in Changjiang estuary waters.

provide a characteristic fingerprint of the water sources. The isotopic composition of modern seawater is close to 0‰ (Clark and Fritz, 1997). In the present study, the water (19–50 m) with the greatest salinity in the estuary had a $\delta^{18}\text{O}$ value of 0‰, while less saline water in the river had a $\delta^{18}\text{O}$ value of -7.1 ‰. As shown in Fig. 3, there was a good positive relationship between the salinity and $\delta^{18}\text{O}$ of the water, which demonstrates that the movement of water mass in the Changjiang Estuary affected the distribution of dissolved ions. The low $\delta^{18}\text{O}$ value of sea water in the estuary suggested that dilution had occurred as a result of freshwater discharge.

2.2. The sources of sulphate in the Changjiang Estuary

The measured $\delta^{34}\text{S}$ values of SO_4^{2-} have a range of 5.3–20.5‰, and $\delta^{18}\text{O}$ – SO_4^{2-} values have a narrow range of 8.0–12.4‰. As indicated by Fig. 4, the SO_4^{2-} could be separated into two major types: freshwater SO_4^{2-} and sea water SO_4^{2-} . The SO_4^{2-} of modern seawater has a very homogenous and well-defined isotopic composition, with a value of +21‰ for $\delta^{34}\text{S}$ and +9.5‰ for $\delta^{18}\text{O}$ (Longinelli, 1989). In the present study, the isotopic compositions of SO_4^{2-} in

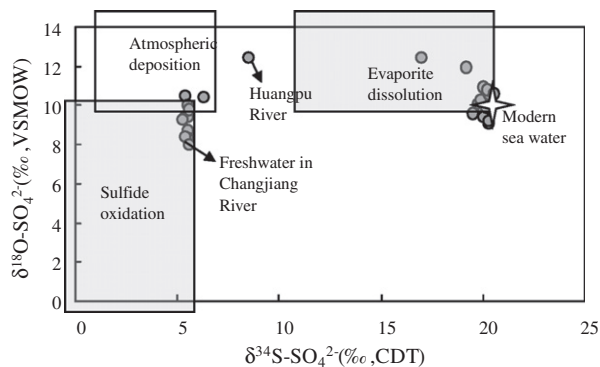


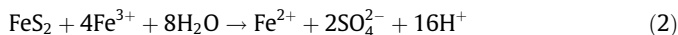
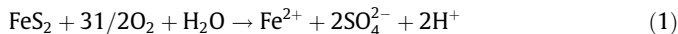
Fig. 4. $\delta^{18}\text{O}-\text{SO}_4^{2-}$ versus $\delta^{34}\text{S}-\text{SO}_4^{2-}$ for waters in Changjiang estuary, China. The isotopic composition of various sources in the diagram (refer to Clark and Fritz, 1997; Krouse and Mayer, 2000; Calmels et al., 2007; Liu et al., 2009).

water samples with high salinity had characteristics similar to modern seawater. In the Huangpu River, the last significant tributary of the Changjiang River before it empties into the East Sea, SO_4^{2-} has $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of 8.5‰ and 12.4‰, respectively. The Huangpu River flows through many cities including Shanghai; thus, SO_4^{2-} in Huangpu River water is mainly derived from atmospheric deposition and anthropogenic inputs.

The dissolved SO_4^{2-} in river water was derived from these major sources, including atmospheric deposition, dissolution of evaporites, sulphide oxidation and mineralization of C-bound S as well as anthropogenic inputs (Pawellek et al., 2002; Rock and Mayer, 2009; Mayer, 2005). Hong et al. (1995) demonstrated that the $\delta^{34}\text{S}-\text{SO}_4^{2-}$ values of rain were below -3‰ in the Changjiang Basin. The O isotope values of atmospheric SO_4^{2-} generally have enriched ^{18}O values due to the high contribution of air O_2 to SO_4^{2-} (Krouse and Mayer, 2000; Jenkins and Bao, 2006). Jenkins and Bao (2006) also showed that the range of $\delta^{18}\text{O}-\text{SO}_4^{2-}$ values was between +10‰ and +20‰ for atmospheric SO_4^{2-} in Baton Rouge, LA in the USA. In the present study, the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of SO_4^{2-} for the mainstream of Changjiang River have a narrow range of 5.3–5.6‰ and 8.6–10.5‰, respectively. Atmospheric deposition might be a minor source of SO_4^{2-} to Changjiang River waters because of low contents of SO_4^{2-} and high $\delta^{18}\text{O}$ values of SO_4^{2-} in precipitation.

The isotopic compositions of gypsum vary based on their geological age (Claypool et al., 1980). The Changjiang watershed is primarily overlain with sedimentary rocks composed of marine carbonates, evaporites and alluvium from Precambrian to Quaternary age (Chen et al., 2002). Evaporites, mainly present in the upper reaches of the Changjiang watershed, release SO_4^{2-} with $\delta^{34}\text{S}-\text{SO}_4^{2-}$ of +11‰ and $\delta^{18}\text{O}-\text{SO}_4^{2-}$ of +8‰ (Liu et al., 2009).

Additionally, rich sulphides are present in coal strata inter-bedded with carbonates in the region, especially in the southern basin of the Changjiang River (Chetelat et al., 2008). The coal has a mean $\delta^{34}\text{S}$ value of -0.3‰ in South China (Hong et al., 1993), which could contribute S to waters after natural oxidation. There are two main processes involved in sulphide oxidation (Taylor et al., 1984; van Everdingen and Krouse, 1985):



The $\delta^{18}\text{O}$ of SO_4^{2-} from sulphide oxidation can be calculated by the fraction f of O_2 vs. H_2O and their respective enrichment factors according to the equation (van Everdingen and Krouse, 1985):

$$\delta^{18}\text{O}_{\text{SO}_4} = f\text{H}_2\text{O}(\delta^{18}\text{O}_{\text{H}_2\text{O}} + \varepsilon^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}) + 0.825f_{\text{O}_2}(\delta^{18}\text{O}_{\text{O}_2} + \varepsilon^{18}\text{O}_{\text{SO}_4-\text{O}_2}) + 0.125(\delta^{18}\text{O}_{\text{H}_2\text{O}} + \varepsilon^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}) \quad (3)$$

The first pathway would lead to O of new SO_4^{2-} derived from air O and water O. The O of new SO_4^{2-} is only derived from water O according to Eq. (2). The isotopic composition of air O is about +23.5‰ (Kroopnick and Craig, 1972; Horibe et al., 1973). In the present study, the $\delta^{18}\text{O}$ of freshwater in Changjiang River has a value of about -7‰. The enrichment factors of $\varepsilon^{18}\text{O}_{\text{SO}_4-\text{H}_2\text{O}}$ and $\varepsilon^{18}\text{O}_{\text{SO}_4-\text{O}_2}$ could be assigned as 4.1‰ and -11.4‰ (Taylor et al., 1984; van Everdingen and Krouse, 1985). Therefore, the $\delta^{18}\text{O}-\text{SO}_4^{2-}$ values would primarily have a range of -10‰ to 10‰. Thus, evaporite dissolution in the upper reach and sulphide and C-bound S oxidation might be the major sources of dissolved SO_4^{2-} for the freshwater of the Changjiang River. Meanwhile, atmospheric deposition and anthropogenic inputs would be the other sources for the Changjiang River.

2.3. The mixing process and factors impacting sulphate in Changjiang Estuary

Sulphate is stable in natural conditions in the river. Therefore, the mean isotopic values and contents of SO_4^{2-} in samples NJ and ZJ (those furthest upstream; Fig. 1) were assigned to the freshwater endmember. Sample 19 from a depth of 50 m had the highest salinity and was designated as the sea water endmember in this study. Fig. 5 shows a mixing model based on the isotope mass balance in Changjiang Estuary following Faure (1986). The results suggest that mixing between freshwater and sea water was the controlling factor for SO_4^{2-} distribution in the Changjiang Estuary. However, the measured $\delta^{18}\text{O}-\text{SO}_4$ does not follow the mixing line. The analytical precision for $\delta^{18}\text{O}$ values was 0.5‰. However, redox processes might affect the $\delta^{18}\text{O}-\text{SO}_4$. Harmful algal blooms occur primarily in a confined region on the inner shelf off the Changjiang River in the East China Sea during May–August. There was also a

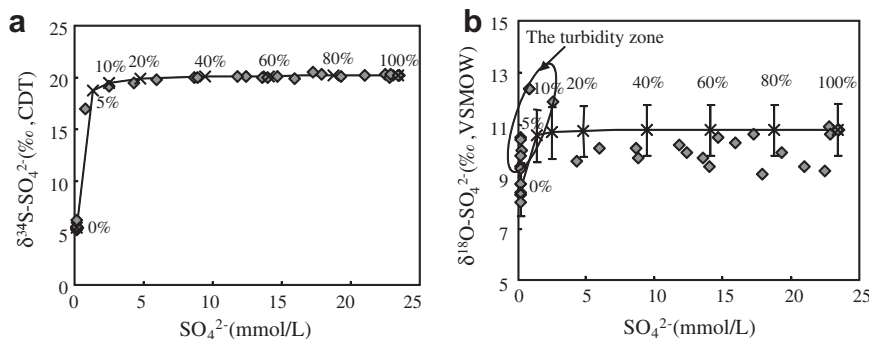


Fig. 5. Mixing models (crosses and lines) calculated with $\delta^{34}\text{S}/\delta^{18}\text{O}-\text{OSO}_4^{2-}$ and SO_4^{2-} concentration (except water of Huangpu River) in Changjiang Estuary following Faure (1986), using endmembers described in the text. Diamonds show measured values.

high chlorophyll-a concentration in this region (Chen et al., 2003). Lewicka-Szczębak et al. (2009) reported that large diurnal variations in the $\delta^{18}\text{O}-\text{SO}_4$ values were observed for summer and spring due to dynamic biochemical transformations occurring in reservoir waters. Sulphur is an important biological element that can be assimilated by biological organisms. The organic S can be oxidized to SO_4^{2-} during summer. This modified SO_4^{2-} would have similar $\delta^{34}\text{S}-\text{SO}_4$ and different $\delta^{18}\text{O}-\text{SO}_4$ values due to the fact that water with more positive $\delta^{18}\text{O}$ values took part in the oxidation reaction. The water samples from the turbidity zone had slightly higher $\delta^{18}\text{O}-\text{SO}_4$ values than others, which might indicate that modified processes would be an important reason for high $\delta^{18}\text{O}-\text{SO}_4$ value in the region.

3. Summary

The salinity and major ions increased from the fresh water end-member to the sea water end-member in Changjiang Estuary. The good positive relationship between salinity and ions as well as $\delta^{18}\text{O}-\text{H}_2\text{O}$ indicated that mixing processes were the major factor controlling the distribution of water and solutes. The SO_4^{2-} concentrations ranged from 0.14 mmol/L to 23.5 mmol/L in this study, while the measured $\delta^{34}\text{S}$ and $\delta^{18}\text{O}-\text{SO}_4^{2-}$ values ranged from 5.3‰ to 20.5‰ and from 8.0‰ to 12.4‰ in Changjiang Estuary, respectively. The dissolved SO_4^{2-} in the Changjiang River mainly derived from atmospheric deposition, evaporite dissolution in the upper reach and sulphide/C-bound S oxidation according to end-member analysis and geological character of basin. The $\delta^{34}\text{S}-\text{SO}_4$ might be affected by mixing processes due to mixing model calculated by isotope mass balance. However, $\delta^{18}\text{O}-\text{SO}_4$ values were not in agreement with the mixing process, which might be affected by biological transformations and redox processes.

Acknowledgments

We thank P. Wu, Y.S. Li, N. An, X.Y. Liu and H.Y. Zheng for their help during the sample collection. We furthermore thank Suzanne Anderson for improving the English of the paper. This work was financially supported by the Natural Science Foundation of China (40721002) and Chinese Academy of Sciences through grants KZCX2-YW-137.

References

- Brenot, A., Carignan, J., France-Lanord, C., Benoit, M., 2007. Geological and land use control on $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of river dissolved sulfate: the Moselle river basin, France. *Chem. Geol.* 244, 25–41.
- Calmels, D., Gaillardet, J., Brenot, A., France-Lanord, C., 2007. Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin: climatic perspectives. *Geology* 35, 1003–1006.
- Chen, C., Zhu, J., Beardsley, R.C., Franks, P.S., 2003. Physical-biological sources for the Dense Algal Bloom over the Western Shelf of the East China Sea. *Geophys. Res. Lett.* 30, 1515–1518.
- Chen, J.S., Wang, F.Y., Xia, J.H., Zhang, L.T., 2002. Major element chemistry of the Changjiang (Yangtze River). *Chem. Geol.* 187, 231–255.
- Chetelat, B., Liu, C.-Q., Zhao, Z.Q., Wang, Q.L., Li, S.-L., Li, J., Wang, B.L., 2008. Geochemistry of the dissolved load of the Changjiang Basin rivers: anthropogenic impacts and chemical weathering. *Geochim. Cosmochim. Acta* 72, 4254–4277.
- Clark, I.D., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York.
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves for sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.* 28, 199–260.
- Faure, G., 1986. *Principles of Isotope Geology*, second ed. John Wiley and Sons, New York.
- Hong, Y., Zhang, H., Zhu, Y., 1993. Sulfur isotopic characteristics of coal in China and sulfur isotopic fractionation during coal-burning process. *Chin. J. Geochem.* 12, 51–59.
- Hong, Y., Zhang, H., Zhu, Y., Piao, H., Jiang, H., Liu, D., 1995. Characteristics of sulphur isotopic composition of meteoric water in China. *Prog. Nat. Sci.* 5, 344–349.
- Horibe, Y., Shigebara, K., Takakuwa, Y., 1973. Isotopic separation factors of carbon-dioxide-water system and isotopic composition of atmospheric oxygen. *J. Geophys. Res.* 78, 2625–2629.
- Jenkins, K.A., Bao, H., 2006. Multiple oxygen and sulfur isotope compositions of atmospheric sulfate in Baton Rouge, LA, USA. *Atmos. Environ.* 40, 4528–4537.
- Kroopnick, P.M., Craig, H., 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. *Science* 175, 54–55.
- Krouse, H.R., Mayer, B., 2000. Sulphur and oxygen isotopes in sulfate. In: Cook, P.G., Herczeg, A.L. (Eds.), *Environmental Tracers in Subsurface Hydrology*. Kluwer Academic Press, Boston, pp. 195–231.
- Lewicka-Szczębak, D., Trojanowska, A., Drzewicki, W., Gorka, M., Jedrysek, M.-O., Jezierski, P., Kurasiewicz, M., Krajniak, J., 2009. Sources and sinks of sulphate dissolved in lake water of a dam reservoir: S and O isotopic approach. *Appl. Geochem.* 24, 1941–1950.
- Liu, C.-Q., Lang, Y.-C., Strauss, H., Chetelat, B., Wang, B.-L., Li, S.-L., Li, J., 2009. Variation in content and isotopic composition of sulfate in Changjiang (Yangtze River) water. *Geochim. Cosmochim. Acta (Goldschmidt Conference Abstracts, A775)*.
- Longinelli, A., 1989. Oxygen-18 and sulphur-34 in dissolved oceanic sulphate and phosphate. In: Fritz, P., Fontes, J.-Ch. (Eds.), *Handbook of Environmental Isotope Geochemistry*. Elsevier, Amsterdam, pp. 219–256.
- Mayer, B., 2005. Assessing sources and transformations of sulphate and nitrate in the hydrosphere using isotope techniques. In: Aggarwal, P.K., Gat, J.R., Froehlich, K.F.O. (Eds.), *Isotopes in the Water Cycle: Past, Present and Future of a Developing Science*. IEA, Netherlands, pp. 67–89.
- Otero, N., Soler, A., Canals, A., 2008. Controls of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in dissolved sulphate: learning from a detailed survey in the Llobregat River (Spain). *Appl. Geochem.* 23, 1166–1185.
- Pawellek, F., Frauenstein, F., Veizer, J., 2002. Hydrochemistry and isotope geochemistry of the upper Danube River. *Geochim. Cosmochim. Acta* 66, 3839–3854.
- Rock, L., Mayer, B., 2009. Identifying the influence of geology, land use, and anthropogenic activities on riverine sulfate on a watershed scale by combining hydrometric, chemical and isotopic approaches. *Chem. Geol.* 262, 121–130.
- Shen, H., He, S., Pan, D., Li, J., 1992. A study of turbidity maximum in the Changjiang estuary. *Acta Geogr. Sin.* 47, 472–479 (in Chinese).
- Taylor, B.E., Wheeler, M.C., Nordstrom, D.K., 1984. Stable isotope geochemistry of acid mine drainage: experimental oxidation of pyrite. *Geochim. Cosmochim. Acta* 48, 2669–2678.
- Van Everdingen, R.O., Krouse, H.R., 1985. Isotope composition of sulphates generated by bacterial and biological oxidation. *Nature* 315, 395–396.
- Zhou, J., Wu, Y., Zhang, J., Kang, Q., Liu, Z., 2006. Carbon and nitrogen composition and stable isotopes as potential indicators of source and fate of organic matter in the salt marsh of the Changjiang Estuary, China. *Chemosphere* 65, 310–317.
- Zhu, G.H., Xu, W.Y., Zhu, D.T., Shi, Q.S., Zhang, J., 2003. Distribution of phytoplankton and water dynamical environmental factors in high red tide occurrence area of Changjiang River estuary. *Chin. J. Appl. Eco.* 14, 1135–1139 (in Chinese).