New Insights at the Molecular Level: The Impact of Dom On Antimony Migration and Enrichment in Water Environments of Antimony

Wanyu Li[1], Jianwei Zhou[1,*], Xingjie Wang[2], Chenxin Feng[1], Haibo Feng[3], Weiqing Zhou[1]

[1]*China University of Geosciences (Wuhan), School of Environmental Studies, 68 Jincheng Road, Wuhan, PR China, wy_li@cug.edu.cn, jw.zhou@cug.edu.cn, fcxaptx4869@163.com, wq.zhou@cug.edu.cn*

[2]*China University of Geosciences (Wuhan), Institute of Geological Survey, 388 Lumou Road, Wuhan, PR China, wangxingjie@cug.edu.cn*

[3]*China University of Geosciences (Wuhan), School of Geography and Information Engineering, 68 Jincheng Road, Wuhan, PR China, haibo_feng@cug.edu.cn*

Abstract

Dissolved organic matter (DOM) significantly influences the migration and transformation of antimony (Sb) in aquatic environments. This study integrated hydrogeochemical analysis with DOM characterization to explore its role in Sb enrichment in mining areas. Results indicated that (1) water contained tryptophan-like proteins and humic substances; (2) CHON and CHO type compounds enhanced Sb enrichment in groundwater, while photodegradable compounds affected Sb in surface water; and (3) non-bioactive compounds and photodegradation products were key to Sb complexation. These findings enhance understanding of Sb biogeochemistry and support pollution control efforts in mining areas.

Keywords: Antimony mining; dissolved organic matter; EEMs; FT-ICR MS

Introduction

Antimony (Sb) is a metalloid element with potential toxicity and carcinogenicity (Lai *et al.* 2022). It and its compounds have a wide range of applications and are important strategic materials. Antimony pollution in the water environment mainly originates from human activities such as mining, smelting, and the combustion of fossil fuels (Quiroz *et al.* 2016). Long-term exposure to high levels of Sb could cause severe damage to the human immune system and development (Wang *et al.* 2020). The U.S. Environmental Protection Agency, the European Union, the World Health Organization, and China have set limits for antimony concentrations in drinking water at no more than 6, 5, 20, and 5 μg/L, respectively (Filella *et al.* 2002).

Dissolved organic matter (DOM) is an important and ubiquitous active component in aquatic ecosystems, containing functional groups such as hydroxyl and carboxyl groups. DOM can serve as a microbial substrate or as an electron donor or acceptor, thereby indirectly affecting the biogeochemical processes of antimony by controlling microbial activities in the water environment (Wang *et al.* 2023). Moreover, DOM can bind with Sb both directly and indirectly. Sb forms bidentate chelating rings with oxygen-containing organic ligands in DOM, such as O = C-OH and C-OH, resulting in the formation of OM-Sb complexes (Tella and Pokrovski 2008). Alternatively, negatively charged organic matter and $Sb(OH)_6^-$ species can interact with metal oxides, forming OM-metal-Sb complexes (Karimian *et al.* 2019). Through these interactions, DOM influences the geochemical processes of Sb. Additionally, under light-induced conditions, the generation of triplet states, phenoxyl radicals from organic matter, and quinone species under dark conditions can all oxidize Sb(III) (Wu *et al.* 2019). However, these studies are all based on laboratory experiments, and the impact of DOM in natural water environments on the biogeochemical cycling of Sb remains unclear.

This study, leveraging water chemistry, DOM spectroscopy, and molecular analysis techniques, aims to elucidate the sources, spectral characteristics, and molecular features of DOM in the water environment of a typical antimony mining area. It analyses the impact of DOM on the migration and enrichment of Sb.

Methods

The samples were collected from Xikuangshan, the largest antimony mine in China, including 10 groups of groundwater and 6 groups of surface water, and the sampling work was completed in June 2022. The aquifer in Xikuangshan is composed of siliceous limestone, with antimony sulfide being the main ore type. The surface was covered with waste rocks and slag piles, which have been disposed of in recent years after being piled up for many years.

The pH, DO, EC, ORP, anions and cations, trace elements, and DOC concentrations in the water environment were tested. For some samples, DOM was analysed using Three-dimensional fluorescence and Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The pretreatment for three-dimensional fluorescence testing involved filtering the samples through a 0.45 μm filter membrane into 40 mL brown glass bottles, followed by the addition of concentrated phosphoric acid of superior purity for preservation. For FT-ICR MS samples, the field samples were filtered through a 0.45 μm filter membrane and then acidified with high-purity hydrochloric acid, followed by storage in the dark at 4°C. The pretreatment was completed within 12 hours, and the steps were as follows: (1) Activation of the SPE column by sequentially washing it with three column volumes of methanol and three column volumes of acidified ultrapure water (pH = 2) at a flow rate of 2 mL/min. (2) Extraction of the water sample with a flow rate controlled at 2 mL/min. (3) Drying of the SPE column by washing it with three column volumes of acidified ultrapure water and removing the moisture from the column using nitrogen gas. (4) Elution of the sample with one column volume of methanol, followed by storage in a brown glass bottle in the dark at -18 °C for submission (Dittmar *et al.* 2008).

The three-dimensional fluorescence results were analyzed using the parallel factor analysis (PARAFAC) method in the DOMFluor toolbox. The FT-ICR MS results were processed using Data Analysis 4.0 (Bruker Corporation).

Results and discussion

Chemical characteristics of the water environment and distribution of antimony

The water environment of the antimony mining area was neutral to slightly alkaline (average pH 7.61), mainly influenced by the limestone aquifer, which neutralized the acidic mine water generated by mining activities. The important ions in the water

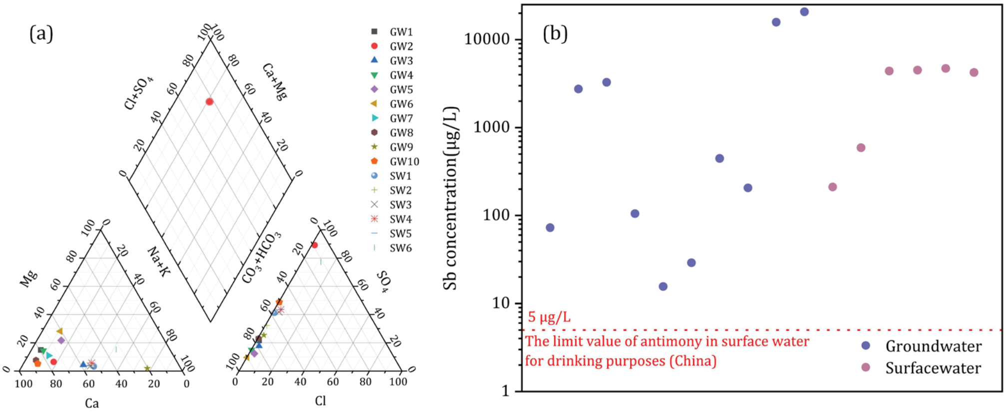

Figure 1 (a) Piper diagram in the water environment of Xikuangshan; (b) Distribution of antimony in the water environment of Xikuangshan.

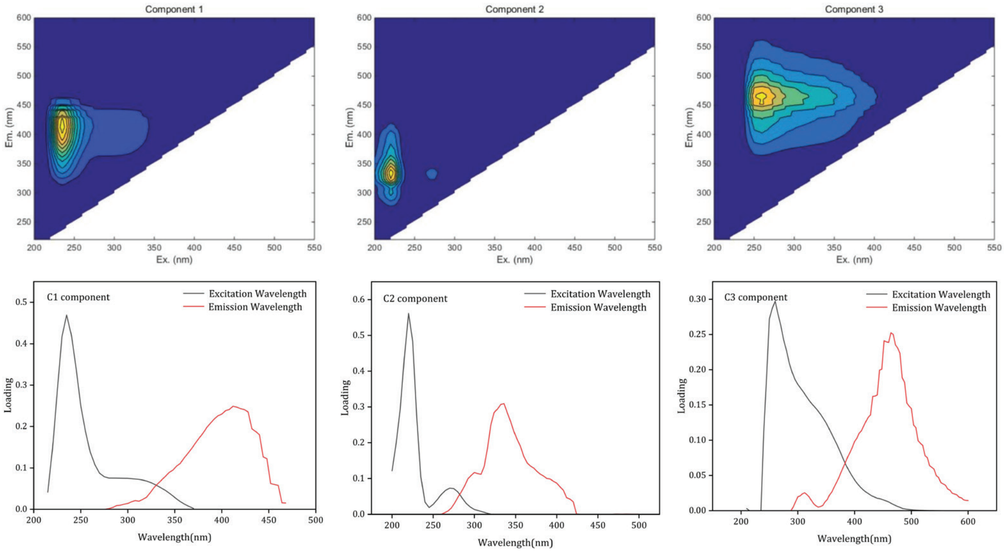

Figure 2 Common components of DOM in the water environment resolved by Parallel Factor Analysis.

environment were Ca^{2+}, Na^+, SO_4^{2-}, and HCO_3^-. The main hydrochemical type of groundwater was primarily Ca-HCO_3, while Na^+ and SO_4^{2-} ions were more prominent in surface water. This was mainly influenced by the leaching of surface waste residues and waste rock piles or the recharge of mine wastewater (Fig. 1a) (Wen *et al.* 2023).

The concentrations of Sb in the water environment of Xikuangshan (15.62–20752.18 µg/L) was far above the limit value for drinking water in China (5 µg/L). The Sb concentration in groundwater had a large degree of dispersion. The surface water samples were taken from a stream, and the Sb concentration increased gradually along the flow direction (Fig. 1b).

Spectral characteristics of DOM and its indicative role in antimony migration and enrichment

Using Parallel Factor Analysis, we could resolve three common components in the water environment of Xikuangshan (Fig. 2). Component C1 was a terrestrial humic-like substance (Ex./Em. 235 nm/412 nm), which was a photochemical product of terrestrial organic matter and represented the smallest molecules generated during the biodegradation process (Coble 1996). Component C2 was a protein-like tryptophan substance (Ex./Em. 220 nm/336 nm), which was an autochthonous product of microbial activity and was associated with the structure of aromatic amino acids (Murphy *et al.* 2008). Component C3 was a terrestrial aromatic humic-like substance (Ex./Em. 260 nm/464 nm), with a larger molecular weight, and it readily formed metal ion-organic complexes with metal ions (Ishii *et al.* 2012).

The average maximum fluorescence intensity relative to the content of the three common DOM components in the water environment followed the order: C1 > C2 > C3, with values of 43.70%, 37.77%, and 18.53%, respectively. The relative distribution of DOM fluorescence components in surface water was more concentrated than in groundwater (Fig. 3a). In groundwater environments with high Sb concentrations (>3 mg/L), the proportions of C1 and C3 components were significantly higher, indicating that humic-like components in groundwater might have influenced the enrichment of Sb through complexation. In contrast, the relative content of the C2 component was significantly lower, suggesting that the binding of tryptophan-like proteins with Sb led to fluorescence quenching, resulting in a notable decrease in fluorescence intensity (Fig. 3b).

In surface water, the relative contents of C1 and C3 components exhibited a trend consistent with Sb concentration along the flow path, whereas the C2 component showed an opposite pattern (Fig. 3c). Similar

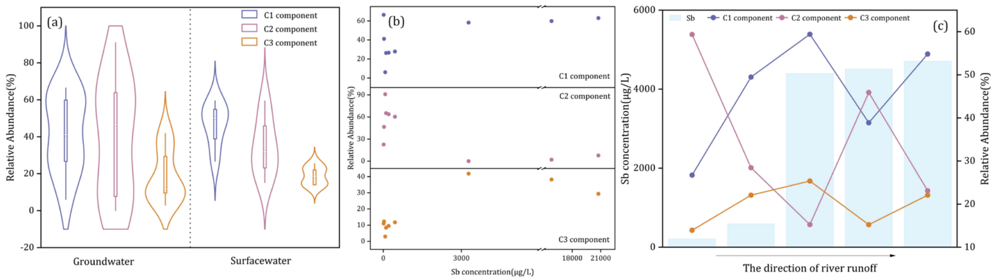

Figure 3 *(a) Boxplot of the relative content distribution of common DOM components in groundwater and surface water environments; (b) Relationship between the relative content of common DOM components in groundwater and Sb concentration; (c) Characteristics of changes in Sb concentration and the relative content of common DOM components along the flow path in surface water runoff.*

to groundwater, the humic-like components represented by C1 and C3 were important complexing species of Sb, and a co-migration process of Sb with these components occurred in surface rivers. Additionally, the fluorescence quenching effect of Sb on tryptophan-like proteins was also significant. At the fourth sampling point, the relative contents of all components changed abruptly due to a shift in the river's surrounding environment from a human activity area to a waste residue and waste rock dumping area, altering the DOM sources and enhancing microbial activity in this region.

Molecular characteristics of DOM and its indicative role in antimony migration and enrichment.

The correlation between individual DOM molecules and Sb concentration in the aquatic environment indicated that Sb enrichment was associated with various types of organic matter (OM). In groundwater, Sb enrichment was primarily related to highly unsaturated compounds, polyphenols, and polycyclic aromatic hydrocarbons (Fig. 4a), with nitrogen-containing compounds being dominant. These compounds were recalcitrant, non-biologically active organic substances that could facilitate Sb migration and enrichment in groundwater through electron shuttling, complexation, and competitive adsorption (Mao *et al.* 2024), while the influence of biological activity on Sb was not significant. The number of OM molecules associated with Sb enrichment in surface water was far lower than in groundwater (Fig. 4b) and was mainly composed of low unsaturated, saturated, and aliphatic compounds, with biological activity playing a more prominent role.

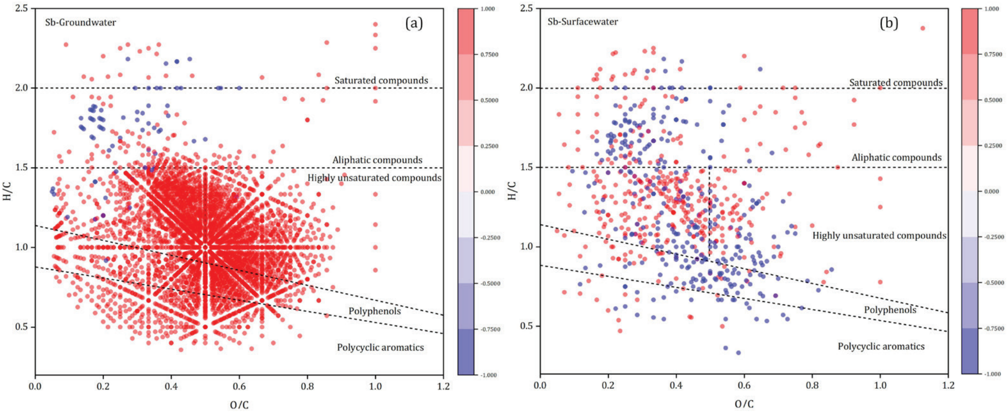

Figure 4 *Correlation between individual molecules and Sb concentration in groundwater (a) and surface water (b).*

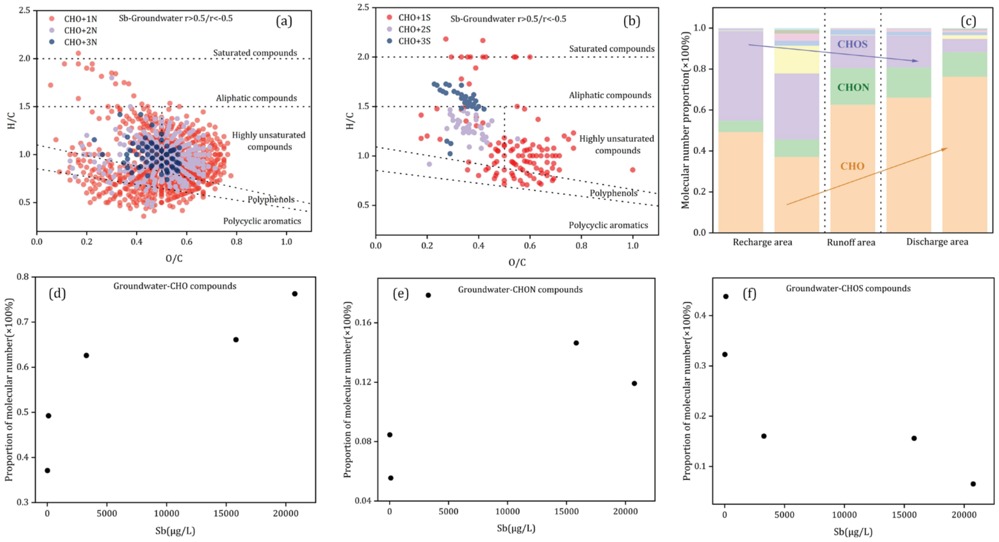

Figure 5 *Correlation between individual molecules of CHO+1N, CHO+2N, CHO+3N compounds and Sb concentration in groundwater (r > 0.5 or r < -0.5) (a), and CHO+1S, CHO+2S, CHO+3S compounds and Sb concentration in groundwater (r > 0.5 or r < -0.5) (b); Stacked bar chart of the proportion of molecular numbers of different elements in different regions of groundwater (c); Correlation between the proportion of molecular numbers of CHO (d), CHON (e), and CHOS (f) compounds and Sb concentration in groundwater.*

In the groundwater environment, the correlation between CHON and CHOS type organic compounds and Sb concentration (Fig. 5a, b) indicated that the recalcitrant, non-biologically active organic compounds that were strongly associated with Sb in the groundwater of the tin mining area were primarily composed of nitrogen- and sulfur-containing organic compounds. Along the groundwater recharge, runoff, and discharge zones, the proportion of CHOS compounds gradually decreased, while the proportion of CHON and CHO compounds gradually increased (Fig. 5c). This suggested that sulfur-containing organic compounds were unfavorable for Sb migration in the saturated zone. When Sb concentrations were relatively low (< 5 mg/L), nitrogen-containing organic compounds facilitated Sb migration, whereas at higher Sb concentrations, CHO type organic compounds played a more significant role in influencing Sb migration or enrichment.

In the surface water environment, the correlation between CHON, CHOS, and CHO type organic compounds and Sb concentration was shown in Fig. 6a, b, and c. The high unsaturation, polyphenol, and polycyclic aromatic components associated with Sb were primarily nitrogen-containing and unsaturated CHO compounds, while the sulfur-containing compounds related to Sb were key components of low-unsaturation, aliphatic, and saturated compounds. During the surface water runoff process, the proportion of CHON and CHO compounds initially decreased and then increased, whereas CHOS compounds exhibited the opposite trend, first increasing and then decreasing. This pattern was mainly influenced by changes in the river's flow path and the inflow of mining wastewater. These findings suggested that, compared to human activity areas, organic matter in solid waste dumping areas, particularly those containing nitrogen and unsaturated functional groups, more effectively complexed with high-concentration Sb, facilitating co-migration.

Conclusions

This study investigated the impact of dissolved organic matter (DOM) on the migration and enrichment of antimony (Sb) in the water environment of an antimony mining area from

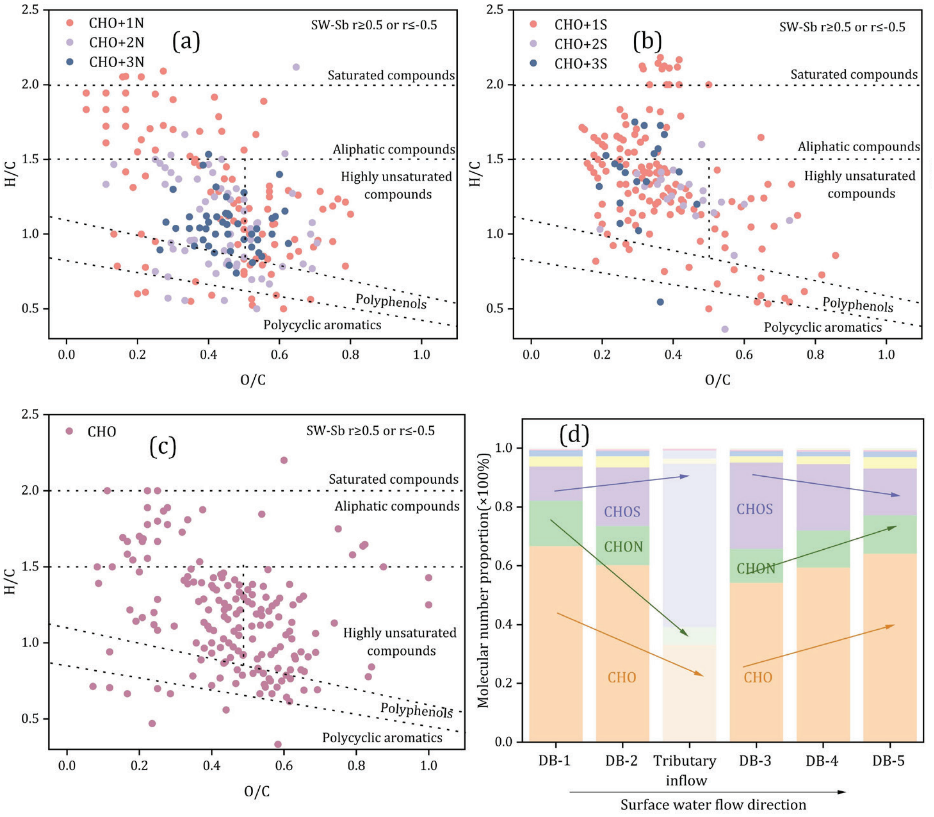

Figure 6 Correlation between individual molecules of CHO+1N, CHO+2N, and CHO+3N compounds and Sb concentration in surface water (r > 0.5 or r < -0.5) (a); CHO+1S, CHO+2S, and CHO+3S compounds and Sb concentration in surface water (r > 0.5 or r < -0.5) (b); CHO compounds and Sb concentration in surface water (r > 0.5 or r < -0.5) (c); and stacked bar chart of the proportion of molecular numbers of different elements along the surface water flow path (d).

the perspectives of water chemistry, DOM spectroscopy, and molecular characteristics. The results showed that the migration and enrichment of Sb in groundwater were associated with recalcitrant, non-biologically active compounds, such as unsaturated compounds, polyphenols, and polycyclic aromatic hydrocarbons, which were primarily composed of nitrogen (N)- and sulfur (S)-containing organic compounds. Compared to CHOS compounds, CHON and CHO compounds were more conducive to the enrichment of Sb in groundwater. In surface water, humic-like components played a crucial role in the complexation and co-migration of Sb, with N-containing functional groups and unsaturated bonds being the primary contributors. Additionally, fluorescence quenching of protein-like components was observed. Overall, complexation was an important mechanism for the enrichment of Sb by DOM in the water environment, with recalcitrant compounds, photodegradation products of organic matter, and protein-like components serving as key complexing species.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (NO. 42030706 and 42077182).

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