

Geochemical characteristics of inorganic sulfur in Shijing River, South China†

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Different inorganic sulfur species distributed in overlying water, pore water and sediment in a heavily polluted river were determined. The concentrations of S^{2-} and SO_4^{2-} in the overlying water were much more than those in the pore water. This result perhaps indicates the S^{2-} was mainly from discharged wastewater, not from sediment resuspension. In the sediments, acid-volatile sulfide, chromium(II)-reducible sulfide, and elemental sulfur were determined by a modified diffusion method. The results indicate that acid-volatile sulfide was the dominant component of the reduced inorganic sulfur, making up about 62% of the total reduced inorganic sulfur.

1. Introduction

Hydrogeochemical analyses of river water provides important information on the biogeochemical cycles of elements.¹ Biogeochemical transformations involving sulfur have attracted increasing attention in recent years. The separation and determination of reduced inorganic sulfur in anoxic sediments are crucial to ecological and geological studies of sulfur cycles.² Numerous studies have been carried out on the distributions and transformations of reduced inorganic sulfur species in freshwater lakes, drain sediments, salt marshes and marine sediments.^{3–6} Previous studies have shown that pyrite (FeS_2) and ferrous monosulfide (FeS) are the two major end products of dissimilatory sulfate reduction in sediments.^{7,8} The reduced inorganic sulfur (RIS) composition in river sediments affects water quality. Sulfate (SO_4^{2-}) and $Fe(III)$ reduction along with the microbially

mediated formation of sulfide minerals can increase alkalinity and reduce metal availability.⁸ However, sedimentary sulfide formation and oxidation can cause a rapid deoxygenation and acidification of the overlying water during sediment resuspension, which represents an environmental hazard.^{9–11} Many procedures have been developed for the determination of acid-volatile sulfur (AVS), elemental sulfur (ES), and chromium-reducible sulfur (CRS) in sediment, and there are many reports of the quantitative measurements of the specificity and efficiency of each procedure for various inorganic and organic sulfur compounds.^{3,7} Because it is an important indicator of geochemical processes for the modality of sulfur in sediment, RIS distributions in marine sediment and coastal salt marshes have been estimated.^{6,12} The knowledge of concentrations and distributions of RIS species in the sediments of heavily polluted municipal rivers is very helpful to understand sulfur geochemical process in past environmental conditions. However, RIS data obtained from fieldwork, such as from river water bodies, are sparse at present, and the distribution, transformation and other geochemical characteristics of RIS in heavily polluted rivers are not well understood.

In this study, we focused on different RIS species contents and their corresponding distribution characteristics for four sites in Shijing River in Guangzhou, South China. This river is typical of

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Environmental impact

Sulfur chemistry in aquatic environments is important not only because sulfur is a major nutrient next to nitrogen and phosphorous, but also because it is an important vehicle for biochemical electron transfer under anaerobic conditions. Sulfur chemistry in aquatic systems, however, is difficult to study operationally due to the sensitivity of reduced sulfur species to atmospheric oxygen and the tedious procedures involved to quantify them. For this reason, field data of sulfur chemistry in aquatic environments is still far from adequate. In this manuscript, we spent quite a bit of effort to study sulfur chemistry in a heavily polluted river and obtained interesting data. Furthermore, geochemical processes of sulfur in river system were discussed.

the heavily polluted rivers in the Guangzhou urban area, and it has been used for sewage drainage for decades. Sulfur pollution, especially odorous volatile organic sulfur compounds, is severe in this river.¹³ In this study, the distributions of AVS, CRS and ES in the river sediment were quantified with a diffusion procedure. Different inorganic sulfur compounds in the river water and the sediment were investigated, and the interference of acid-soluble ferric minerals on the AVS analysis of the specimen sulfides and the sediment were studied using the cold diffusion procedure. Because of their important role in the transformation of different inorganic sulfur species, different Fe species were also evaluated.

2. Methods and materials

2.1 Site description

The Shijing River is a heavily polluted river with a chemical oxygen demand (COD_{Cr}) ranging from 120 mg l⁻¹ to 197 mg l⁻¹. The water quality often presents a well-regulated variation with the rising and falling tides of the Pearl River twice a day.¹³ Four representative sampling sites were selected in the Shijing River. These sites were named, from downstream to upstream, 1#, 2#, 3#, and 4# (Fig. 1). These four sites are characterized by a black and odorous water body, and some odorous volatile organic sulfur compounds have already been identified.¹³ The sediment and water samples were collected during dry days, allowing the overlying water depths and water quality to maintain good stability.

2.2 Sample collection and handling

All sampling equipment and storage containers were cleaned with distilled water before use, and all samples were collected without disturbing the sediment-water interface. The dissolved oxygen (DO) concentrations and the Eh values in the overlying water were measured at each site. The water samples and sediments were collected mid-stream. All water samples were collected in 500 ml polypropylene vials from mid-stream, at about 0.2 m below the water surface. The vials were completely filled with water (no bubbles or headspace), sealed with gastight

screw caps, and kept in an icebox under an inert (N₂) atmosphere. These samples were analyzed within 48 h. The surface sediments were collected using a stainless steel spatula and were immediately placed in 250 ml polypropylene vials. The vials were fully filled with sediment and sealed with gastight screw caps. Before analysis, all sediment samples were homogenized by mixing with a glass rod under a stream of N₂. All samples were immediately frozen under 0 °C in an adiabatic box before the analysis was performed.

2.3 Apparatus and analytical reagents

To avoid the risk of oxidation during analysis, an anaerobic apparatus for the diffusion procedure was conducted. This anoxic apparatus (box) was made of a glass plate that was 120 cm, 70 cm and 80 cm as length, width and height, respectively. The box was absolutely hermetic. Before operation, all flasks, samples, reagents, stoppers, Teflon connecting pipes and other corresponding apparatus were put into the anaerobic box and were fluxed with pure nitrogen. A pair of long-sleeved rubber gloves was fastened to two holes (15 cm diameter) on the front wall of the box to ensure obturation and to operate the experimental procedures freely.

The preparation of the reagents was same as the reagents described in detail by Hsieh and Yang.⁷ All chemical reagents were of analytical grade. Amalgamated zinc, Zn (Hg) (50 : 50), was purchased from APL Engineered Materials, Inc. (Urbana, Illinois, USA). Pyrite was purchased from Yunfu Pyrite Enterprise Group Corporation (Yunfu, China). The total organic carbon (TOC) of the water bodies and the pore water samples were analyzed using a TOC-Vcph (Shimadzu, Japan) after being filtered by 0.45 µm membrane filters (Whatman International Ltd., Springfield Mill, UK). Measurements of the DO dissolved in the water bodies were conducted *in situ* with a YSI550A handheld dissolved oxygen system (TechTrend International Limited, USA). The pH and Eh of the water bodies and sediment were measured using a Portable pH/mV/temperature meter (HI8424 from Kernco Instruments Co., Inc., Japan) in the field.

2.4 Separation of AVS, CRS, ES in sediment

The separation and determination of AVS, CRS and ES were conducted following the diffusion procedure described by Hsieh and Shieh.² This step involved the sequential separation of AVS, CRS and ES from sediment samples that had been stored frozen under N₂ for no longer than one week. Briefly, the AVS, CRS and ES were separated sequentially by 6 M HCl (18 h), acidic Cr(II) (48 h) and Cr(II) plus N, N-dimethylformamide (DMF, 24 h), respectively, under a pure N₂ atmosphere (in an anaerobic apparatus) at ambient temperature (25 °C). During operation, the velocity of the N₂ flow in the anoxic apparatus was controlled at 1 L min⁻¹ to maintain an anaerobic environment. The liberated H₂S was passively trapped in an alkaline Zn solution (20% ZnOAc). The quantity of S for each solid-phase RIS species involved in the trapped ZnS was determined by iodometric titration.

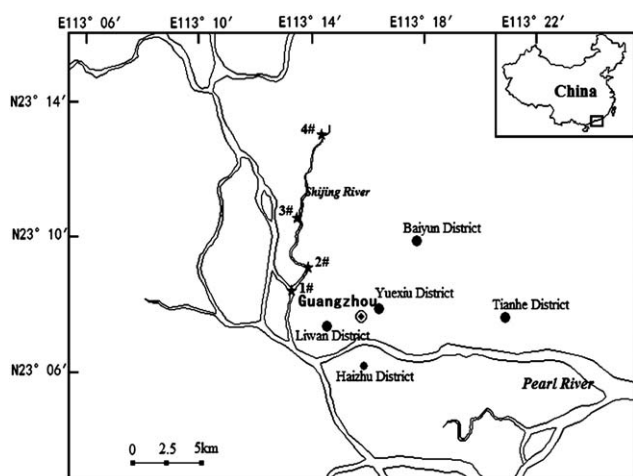


Fig. 1 Detailed locations of sampling sites and Shijing River.

2.5 Analysis of S^{2-} , SO_4^{2-} , Fe^{2+} , and Fe^{3+} in water bodies and pore water samples

The water body samples were analyzed directly. The pore water was separated from a sub-set of samples by transferring the bulk sediment into 50 ml acid washed polycarbonate centrifuge tubes under a nitrogen atmosphere (in the anaerobic box). The tubes were purged with N_2 prior to transfer and centrifuged at 3000 RPM for 30 min followed by vacuum filtration with disposable 0.45 μm membrane filters. All filters were rinsed with 1% HCl and deionized distilled water immediately prior to use. The pore water retrieval and filtration were performed in less than 30 s for each sample to minimize oxidation of the reduced pore water species. All parameters were determined by the corresponding methods.¹⁴ Briefly, Fe^{2+} was measured spectrophotometrically with phenanthroline method at 510 nm. The total iron [Fe(II) plus Fe(III)] was determined by the use of a Ferrozine reagent with 1% hydroxylamine-hydrochloride as the reducing agent. Fe(III) was calculated as the difference between total Fe and Fe(II). The concentrations of SO_4^{2-} were estimated by barium chromate spectrophotometry. The sulfides (including H_2S , HS^- , S^{2-} , and aqueous sulfide complexes collectively denoted as S(II)) were immediately preserved using ZnOAc prior to determination by the methylene blue method.¹⁵ The precision and accuracy of the analytical methods is illustrated in Table 1.

3. Results and discussion

3.1 Distributions of S^{2-} , SO_4^{2-} , Fe^{2+} and total iron in overlying water and pore water

During sampling, the DO of the river water ranged from 0.12 to 0.44 mg l^{-1} (Table 2), and the TOC ranged from 10.28 to 31.92 mg l^{-1} . The data suggested a declining trend in the water quality of this river when compared with a previous study.¹³ Furthermore, the river water was obviously anoxic, and the DO values indicated a transition from suboxic conditions in the river mouth to more reducing conditions upstream from sampling sites 1# to 4#. Large quantities of domestic sewage and commercial wastewater are emptied into Shijing River without any treatment, while little clean water is discharged upstream, exhausting the oxygen and resulting in a DO close to zero.

The concentrations of S^{2-} in the river water ranged from 0.32 to 4.97 mg l^{-1} (Table 3). The maximum concentration increased about five times compared with last year's concentration range of 0.27 to 0.94 mg l^{-1} .¹³ The pore water concentrations of S^{2-} ranged from 0.01 to 2.63 mg l^{-1} , lower than those detected in the overlying water at the corresponding sites. This result perhaps indicates that the S^{2-} was mainly from discharged wastewater, not from sediment resuspension; if not, then there must be a large quantity of S^{2-} dissolved in the pore water that is fixed by the sediment through unknown chemical reactions. Overall, the

concentrations of S^{2-} in the overlying water and the pore water have an obviously increasing trend from sampling sites 1# to 4#. This trend corresponds with the variability of DO.

For sulfate, the concentrations of SO_4^{2-} ranged from 55.7 to 73.85 mg l^{-1} in the overlying water and 8.99 to 24.85 mg l^{-1} in the pore water. Obviously, the concentrations of SO_4^{2-} decreased about six times from the overlying water to the pore water. For the whole river, the maximum concentrations of SO_4^{2-} occurred at sampling site 2# for both the overlying and pore water at 73.85 and 24.85 mg l^{-1} , respectively. This phenomenon perhaps indicates that there may be an SO_4^{2-} discharge source near site 2#. This concentration level is similar to that of the Serchio River (12–94 mg l^{-1}).¹⁶ However, in the Serchio River, the COD values range between 0 and 8 mg l^{-1} , thus denoting good quality water; but in the Shijing River, the COD values were over 100 mg l^{-1} , which is much higher than the acceptable values for water for human consumption.¹⁶ Usually, S^{2-} and SO_4^{2-} are the two main inorganic sulfur species, and their distributions can be used to indicate redox conditions in water environments. For both overlying water and pore water, most of the concentrations of SO_4^{2-} were higher by one to two orders of magnitude than the S^{2-} in the same sampling site at the studied river. Apart from the direct input from small branches of river, this high SO_4^{2-} content may be due to the oxidation of reduced sulfur compounds within the overlying alluvial loam. Because the hydrochemical conditions within the aquifer are generally reducing, the SO_4^{2-} reduction is likely to be the major SO_4^{2-} sink.¹⁷ The values of $\text{S}^{2-}/\text{SO}_4^{2-}$ for the overlying water ranged from 0.005 to 0.084, indicating that the SO_4^{2-} availability may be limiting S^{2-} formation at the study sites. However, at sampling site 4#, the value of $\text{S}^{2-}/\text{SO}_4^{2-}$ in the pore water reached 0.364, which is more than four times higher than that in overlying water. The SO_4^{2-} content of the pore water at this site dropped to less than 7.22 mg l^{-1} , while the accompanying S^{2-} concentrations were high (2.63 mg l^{-1}). This phenomenon may indicate a large quantity of S^{2-} was produced through dissimilatory sulfate reduction in the sediments.^{8,18} The much lower SO_4^{2-} concentrations in the pore water near the sediment surface are consistent with dissimilatory SO_4^{2-} reduction. In this process, S(VI) acts as an electron acceptor in the oxidation of a range of organic substrates.¹⁸

The concentrations of S^{2-} , for example, in the pore water were far lower than those in the overlying water at each corresponding

Table 2 Parameters of water quality in different sampling sites

	pH	ORP (mV)	DO (mg l^{-1})	T ($^{\circ}\text{C}$)	TOC (mg l^{-1})
1#	7.59	−29.7	0.44	24.9	10.28
2#	7.19	−14.0	0.14	23.9	31.92
3#	7.43	−28.7	0.12	22.2	20.18
4#	7.25	−17.1	0.13	23.6	28.26

Table 1 Precision and accuracy of the analytical methods (Unit: %)

Items	Water				Sediment		
	S^{2-}	SO_4^{2-}	Fe^{2+}	Total iron	AVS	CRS	ES
RSD	<12	0.15–6	0.33–1.0	0.18–1.2	3.1–9.6	1.9–8.1	1.2–7.3
Recovery rate	80–97	97–106	97–102	99–100	83–94	91–97	89–101

Table 3 Items of overlying water and pore water at different sites (Unit: mg l⁻¹)

	Items	1 [#]	2 [#]	3 [#]	4 [#]	Average
Overlying water	S ²⁻	0.32	4.01	4.65	4.97	3.49
	SO ₄ ²⁻	64.51	73.85	55.70	59.05	63.28
	S ²⁻ /SO ₄ ²⁻ ^a	0.005	0.054	0.083	0.084	0.057
	TOC	10.28	31.9	20.18	28.26	22.66
	Fe ²⁺	0.31	1.65	1.67	4.33	1.99
	Total iron	1.82	2.22	1.37	6.57	2.99
Pore water	S ²⁻	0.01	0.02	1.41	2.63	1.02
	SO ₄ ²⁻	8.99	24.85	21.06	7.22	15.53
	S ²⁻ /SO ₄ ²⁻ ^a	0.001	0.001	0.067	0.364	0.11
	TOC	36.06	56.72	80.53	112.17	71.37
	Fe ²⁺	0.54	12.09	0.54	0.54	3.43
	Total iron	2.09	16.74	1.09	0.64	5.14

^a no dimension unit.

site. This result gives credence to the hypothesis that the sedimentary RIS pools were low due to iron limitation.¹⁹ The TOC of the pore water in the tested river was 71.37 mg l⁻¹ (Table 3), meaning there was a great amount of organic matter accumulated in the sediment. Werne *et al.* found that organic sulfur was derived primarily from pore water sulfide, with minor contributions from primary bio-sulfur (*e.g.*, in the proteins derived from algae and bacteria).²⁰ They also found that the pore water sulfide was the ultimate source of the reduced sulfur for incorporation into organic matter. Furthermore, the reactive sulfur intermediates, such as ES or polysulfides, react directly with organic matter, and these sulfur species are likely formed through the partial oxidation of sulfide by anaerobic sulfide-oxidizing microbes living in the sediments.²⁰ The dissolved Fe²⁺ in the overlying water and pore water ranged from 0.31 to 4.33 mg l⁻¹ and 0.54 to 12.09 mg l⁻¹, respectively. In contrast, these concentration levels were found to be lower than the distributions of Fe²⁺ (generally >112 mg l⁻¹) in coastal acid sulfate soil landscapes.¹⁸ In this study, a large portion of reactive Fe²⁺ may have been transformed into FeS or pyrite. Due to the low content of metals in the sediment, the reduced sulfur pools are cycled rapidly with chemical and biological reoxidation at oxic–anoxic boundaries as a major sink.¹⁹ The sulfate reduction and formation of sulfide minerals in drain sediments may improve water quality by sequestering Fe and other metals and by increasing alkalinity.⁸ The accumulation of SO₄²⁻ reduction products, such as AVS and FeS₂, may also represent an environmental hazard capable of deoxygenating and acidifying the overlying water during sediment re-suspension events.^{4,10}

3.2 Distribution of AVS, CRS and ES in sediment

In the surface sediment, AVS was the dominant RIS compared with CRS and ES at all sites. The AVS ranged from 9.3 to 47.4 μmol g⁻¹ (Table 4). In comparison, near the estuary of the Pearl River, the sediments usually contained lower AVS. The concentration of AVS at site 1[#] was lower than the other sites. However, these AVS levels are lower than those distributed in natural estuarine and marine sediments (about 90 μmol g⁻¹), though they are consistent with the findings of Bush.^{4,21} The present study has shown that the concentration of DO in

the overlying water at sampling site 3[#] had the lowest value (0.12 mg l⁻¹), but it had the highest concentration of AVS (47.44 μmol g⁻¹). This result indicates that AVS oxidation may cause severe deoxygenation and acidification in receiving waterways due to sediment resuspension during flood events.¹⁰ The detailed concentrations and proportions are listed in Table 4.

In comparison, unpolluted freshwater sediments usually contain < 15 μmol g⁻¹ AVS, with low SO₄²⁻ availability, limiting the development of greater AVS levels.²² Previous studies examined drain sediments from acid sulfate soil landscapes have focused on AVS and FeS₂–S pools.⁴ The accumulation of AVS is often limited by progressive transformation to FeS₂.²¹ The AVS levels reported here were 9.3 to 47.4 μmol g⁻¹ (Table 4). These levels are much higher than those found in Shenzhen Bay, South China (7 μmol g⁻¹), though they are consistent with the Pearl River estuary coastal zone (15.39 μmol g⁻¹).^{23,24}

The composition of RIS in the surface sediment was dominated by AVS (51–81% of the total RIS) and was highest in sampling site 3[#] (47.44 μmol g⁻¹) and lowest in sampling site 1[#] (9.32 μmol g⁻¹). ES only accounted for 3–6% of the total RIS comparing with other RIS pools. The maximum sulfate reduction rates were two to five times higher in the muddy sand than in the sandy sediments, and the muddy sand had up to an order of magnitude more RIS than the two sandy sediments.¹⁹ Although temperature controls biochemical processes, the overall control is more complex due to the simultaneous influence of other factors such as availability of organic matter and oxidation level of surface sediment.¹⁹ The CRS concentrations in the sediments examined here ranged from 7.63 to 24.22 μmol g⁻¹ (Table 4). These concentration levels are lower than those in drain sediments from acid sulfate soil landscapes (10–815 μmol g⁻¹).¹⁸ The proportion of total reduced inorganic sulfur (TRIS) as CRS decreased from upstream to downstream, except at sampling site 3[#].

The concentration of ES ranged from 0.63 to 3.64 μmol g⁻¹ (Table 4), which is low in comparison with previous reports of approximately 2–50 μmol g⁻¹ in estuarine and marine sediments and nearly 10 μmol g⁻¹ in mine pit lake sediments.^{25,26} It should be noted that these previously reported ES concentrations were in sediments containing substantially higher ES contents than in heavily polluted river sediments. However, Thode-Andersen and Jørgensen reported that ES may be the most abundant short-term SO₄²⁻ reduction product in near-surface sediments.²⁷ This is the result of incomplete oxidation of pore water sulfide (produced

Table 4 Distributions of sulfur species in river Sediments (Unit: μmol g⁻¹)^a

	1 [#]	2 [#]	3 [#]	4 [#]	Average
AVS	9.32	29.53	47.44	43.91	32.55
CRS	7.63	24.22	8.51	22.52	15.72
ES	0.63	3.64	2.81	2.33	2.35
TRIS	17.58	57.39	58.76	68.76	50.62
AVS/CRS ^b	1.22	1.22	5.58	1.95	2.49
AVS/TRIS ^b	0.53	0.51	0.81	0.64	0.62
CRS/TRIS ^b	0.43	0.42	0.14	0.33	0.33
ES/TRIS ^b	0.04	0.06	0.05	0.03	0.05

^a TRIS: total reduced inorganic sulfur (AVS + CRS + ES). ^b no dimension unit.

via SO_4^{2-} reduction) by the O_2 , Fe^{3+} and Mn^{4+} species.²¹ Future research is needed to assess the relative importance of O_2 , Fe^{3+} , and Mn^{4+} as electron acceptors during the oxidation of AVS to ES. ES comprised substantial proportions (up to 62%) of RIS in the near-surface sediments of drain sediments associated with acid sulfate soils.¹⁸ King found that ES comprised more than 90% of short-term SO_4^{2-} reduction end products in a 0–4 cm depth interval of South Carolina salt marsh sediments.²⁸ King also found that this proportion decreased to less than 20% at depths greater than 8 cm below the sediment surface.²⁸ Similarly, Thode-Andersen and Jørgensen found that ES exceeded the AVS concentration and was also the most abundant short-term end product of SO_4^{2-} reduction in a 0–1 cm depth interval of coastal marine sediments from Denmark.²⁷ However, in this study, the results were completely opposite to previous reports. ES only accounted for 3–6% of the total RIS, which is much lower than the proportion of AVS (51–81%) and CRS (14–43%). This phenomenon perhaps indicates that the reaction of the oxidation of AVS to ES in sediments is difficult in a heavily polluted river for an extreme anaerobic water environment and that ES is not the dominant RIS of short-term SO_4^{2-} reduction end products in heavily polluted river sediments.

The ratio of AVS to CRS is an indicator of bottom water oxygenation conditions.²⁹ Because sulfur occurring as FeS is in a lower oxidation state than sulfur as pyrite, an increase in this ratio often indicates a depositional environment lower in free oxygen.³⁰ Furthermore, the AVS/CRS ratio often provides a more reliable proxy for bottom water oxygenation conditions than the degree of pyritization because it is less affected by change in available Fe.²⁹ In the tested river sediments, the values of AVS/CRS ranged from 1.22 to 5.58 at the different sites with an average value of 2.49. The highest AVS/CRS ratio was found at site 3[#] (5.58), indicating the surface sediment of 3[#] is in an area of relatively strong reducing conditions. The lowest DO in the overlying water at site 3[#] (0.12 mg l⁻¹) proved this result. Gagnon *et al.* suggested that CRS to AVS ratios less than three indicate inefficient conversion of AVS to CRS, and they hypothesized that this may be related to high levels of reactive Fe.³¹ In this study, the ratios of CRS to AVS ranged from 0.18 to 0.82 (the reciprocal of the AVS/CRS value). All ratios are far lower than three, thus indicating that there must be low levels of reactive Fe in the sediment, based on the above theory.

4. Conclusions

The concentrations and compositions of several species of inorganic sulfur were determined in the overlying water, pore water and sediments of a heavily polluted river in South China. It was shown that the average concentration of S^{2-} in the overlying water reached 3.49 mg l⁻¹, but it was only 1.02 mg l⁻¹ in the pore water. This result suggests that there must be a large quantity of S^{2-} dissolved in the pore water and fixed by the sediment through certain chemical reactions. In sediment, ES only accounted for 3–6% of the total RIS, which perhaps indicates that the reaction of the oxidation of AVS to ES in sediments is difficult in a heavily polluted river for an extreme anaerobic water environment and that ES is not the dominant RIS of short-term SO_4^{2-} reduction end products in heavily polluted river sediments.

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