

## Blackening and Odorization of Urban Rivers: A Bio-geochemical Process

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**One sentence summary:** this review comprehensive summarize the complex biogeochemical process in blackening and odorization of urban rivers.

## **ABSTRACT**

Urban rivers constitute a major part of urban drainage systems, and play critical roles in connecting other surface waters in urban areas. Black-odorous urban rivers are widely found in the developing countries experiencing rapid urbanization. The mismatch between urbanization and sewage treatment is thought to be the reason of the blackening and odorization phenomenon. This phenomenon is likely a complex bio-geochemical process of which the microbial interactions with the environment are not fully understood. Here, we provide an overview over the major chemical compounds, such as iron and sulfur, and their bio-geochemical conversions during blackening and odorization of urban rivers. Scenarios explaining the formation of black-odorous urban rivers are proposed. Finally, we point out knowledge gaps in mechanism and microbial ecology that need to be addressed to better understand the development of black-odorous urban rivers.

## INTRODUCTION

Rivers and lakes serve urban populations as water resource and drainage systems. They play important roles as domestic, industrial and agricultural water resources. Urban rivers are also a convenient way of transportation and have, as centers for aquatic recreation, impact on property prices and city development decisions. However, rapid urbanization caused by fast population growth often does not keep pace with construction of sewage treatment systems, resulting in visible and smellable pollution of urban rivers. Historically, rapid urbanization has always been accompanied by urban river pollution. In London 1855, the English scientist and inventor Michael Faraday wrote to the Times of London after his passage across the river Thames: “The smell [of the river] was very bad, and common to the whole of the water; it was the same as that which now comes up from the gully-holes in the streets; the whole river was for the time a real sewer” (Faraday 1855). More recently, many developing countries experienced the problem of polluted urban rivers as well. River pollution’s most visible manifestation is a change in color, usually black, often accompanied by strong unpleasant odors.

In China, after the first report of blackening and odorization of the Huangpu River in 1983 (Gu and Cai 1983), similar phenomena were observed in other urban rivers as well as their tributaries throughout the whole country, e.g. the Suzhou River in Shanghai (Ying *et al.* 1997), the Pearl River Delta, in particular in Guangzhou (Luo 2001), and the Weigong River in Shenyang (Li *et al.* 2003). By the end of 2016, there were around 1,880 identified black-odorous urban rivers in 295 Chinese cities, and 64% of those rivers were located in coastal areas of southern China

(Zhu 2016). The Chinese government recently released a national plan called “Action Plan for Prevention and Treatment of Water Pollution” for water pollution control, and set targets for cleaning up polluted urban rivers. Nevertheless, only 45% of the identified black-odorous urban rivers were under or had been finished treatment at that time (Kong 2016).

Better pollution control is in urgent need to address blackening and odorization of urban rivers. However, it is often unclear what the exact reasons for the observed phenomena are. To better allocate resources for effective pollution control, it is necessary to identify the sources of pollution. A thorough understanding of the bio-geochemical processes underlying formation of black-odorous rivers is the first step, not only to apply effective pollution control but also to monitor the success of these measures and make adjustments if necessary. Organic pollutants from untreated waste streams or other nonpoint sources, e.g. agricultural and urban storm water runoffs (Mccoy *et al.* 2015), along the river bank are believed to trigger blackening and odorization of urban rivers (Zhou *et al.* 2000; Fang *et al.* 2012; Zhu 2016). The common understanding of the process is that high organic loading quickly depletes dissolved oxygen, leading to anaerobic conditions. Then, anaerobic microorganisms degrade dissolved organics, such as carbohydrates, fatty acids, proteins, etc. into smaller molecules including odorous organic acids and reduced sulfur compounds, e.g. H<sub>2</sub>S and organic sulfides. These small molecules may then further react with minerals in the water and sediment, mediated by microorganisms to form black precipitates (Stahl 1979; Ji *et al.* 2016).

Inorganic fertilizer pollution, such as phosphorous and nitrogen, is involved in odorization of urban rivers as well. They, for example,

accelerate growth of phototrophs, a phenomenon known as eutrophication. In summer 2007, an odorous tap water crisis occurred in Wuxi, China, in which odorous volatile sulfide compounds, including methyl thiols, dimethyl sulfide and dimethyl disulfide, were produced in the river from the decomposition of massive cyanobacterial blooms (Zhang *et al.* 2010). While such events are well documented for seawater environments (Yan *et al.* 2002), freshwater blooms were less monitored in China. For example, the notoriously cyanobacteria-infested Lake Taihu in China experienced major blooms about every 3 years between 1960 and 1996 with increasing magnitude and frequency in recent years due to massive fertilizer pollution (Chen *et al.* 2003).

In this review, we focus on the key mechanisms and compounds involved in blackening and odorization of urban rivers. Based on the most relevant bio-geochemical processes, we propose scenarios to describe the formation of black-odorous urban rivers. We describe microbial communities in polluted and pristine freshwater systems which catalyze these processes. Lastly, we discuss challenges and possible strategies to control blackening and odorization, and propose key questions to be addressed in future studies.

## **ELEMENTS/COMPOUNDS CONTRIBUTE TO BLACKENING AND ODORIZATION OF URBAN RIVERS**

Large quantities of anthropogenic pollutants, both organic and inorganic, destabilize urban river ecosystems. Composition and concentration of organic matter in water, soil, and sediment varies (Table 1). Biorecalcitrant humus, that is dominating fully decomposed organic matter,

accounts for  $\geq 40\%$  of total organic matters present in urban rivers (Thurman *et al.* 1985). These humic substances are resistant to further microbial degradation, and form black chelates with metal ions (Davies *et al.* 1998; Fiedler *et al.* 2002).

The abundance of inorganic substances in urban river sediments is similar to that in the Earth's crust and soil (Table 2). Dominant metallic elements in river waters are iron, magnesium, aluminum, and manganese, which originate from major clay minerals in sediments (Table 3; Abdullah *et al.* 2014). Abundant metals in the Earth's crust like Fe and Mn are major blackening ingredients in black-odorous urban rivers (Table 2; Table 3; Metzger *et al.* 2014). Other major metallic elements, e.g. Al, Ca, Mg and Zn, are either in white color when forming chemical compounds or their too low redox potentials ( $\leq -760$  mV in standard conditions) prohibit participation in natural redox processes. Sulfur, nitrogen and carbon are the three major non-metallic elements contributing to stench of urban rivers through formation of volatile compounds, e.g. H<sub>2</sub>S, organic sulfides, NH<sub>3</sub>, amines, and short chain fatty acids (Table 2; Table 3; Ginzburg *et al.* 1999; Bentley and Chasteen 2004; Ebil *et al.* 2014). In coastal areas, urban rivers are often tributaries to tidal rivers with high concentrations of sulfate and magnesium (Latha and Rao 2012). Additionally, the metallic elements, e.g. Fe, Mn and Mg are mobile between sediment and water phase, sometimes mediated by microorganisms (Rzepecki 2012). Exchange rates are accelerated by organic pollution of urban rivers (Odigie *et al.* 2014).

# BIOGEOCHEMICAL TRANSFERS OF THE KEY ELEMENTS INVOLVED IN WATER BLACKENING AND ODORIZATION

## Black color formation via metal precipitates

Black matter in urban rivers comprises black metallic precipitates, as well as precipitates of brown, green, or other non-black colors, which together form a dark color. In O<sub>2</sub>-depleted surface waters, metals precipitate with sulfide and stain the water black (Fig. 1; Table 4; Nealson and Little 1997; Metzger *et al.* 2014). Common metals such as iron and nickel form black or dark sulfides. Iron, nickel, and copper sulfides are the thermodynamically most favorable precipitates (Table 4). Stahl (1979) investigated a black water lake in Illinois and demonstrated that ferrous sulfide was responsible for the black color. Mixed minerals such as copper-iron sulfides have been observed as well, for example, in the Danube River Basin (Brankov *et al.* 2012). Copper and other heavy metal precipitates were also detected in the Pearl River Estuary, China (Fang *et al.* 2005) as well as the Reno River watershed, Italy (Ferronato *et al.* 2013). In reduced environments, Mn exists as soluble Mn<sup>2+</sup>, due to its low affinity to sulfur and does not precipitate (Nealson and Little 1997).

While iron sulfide formation is spontaneous, microorganisms of *Geobacter*, *Geothrix*, *Rhodospirillum*, *Shewanella*, etc. can harvest the released energy for their cell growth from the processes (Fig. 1; Lovley 1991). Thermodynamically, formation of FeS is favored followed by FeS<sub>2</sub> and Fe<sub>3</sub>S<sub>4</sub> (Table 4). Greigite (Fe<sub>3</sub>S<sub>4</sub>) is formed in excess of sulfide. Elemental sulfur (S<sup>0</sup>) and polysulfide (S<sub>n</sub><sup>2-</sup>) formation are thought to be the

intermediate steps leading to pyrite and greigite (Table 4; Rickard 1975; Luther 1991). Similar to bio-geochemical transfers in marine sediments, the FeS and FeS<sub>2</sub> as well as other metals play central roles in the sulfur cycle in urban rivers (Schipper and Jørgensen 2002). That is, metals and especially abundant iron, are reduced by organic pollutants, such as volatile fatty acids (VFAs such as acetic, butyric and propionic acids), or other reducing equivalents (Table 4). If iron then again enters oxidizing zones, for example by currents or shift of oxic zones, it can be re-oxidized by dissolved oxygen, nitrate, or manganese oxides. Iron oxides, such as goethite, can also be reduced biologically. Humic substances enhance the bioavailability of insoluble Fe(III) oxides as electron acceptors and therefore improve the thermodynamics of biological iron reduction (Lovley *et al.* 1996; Lovley *et al.* 1998). Quinone moieties in humic substances serve as electron shuttles in Fe(III)-respiring microorganisms, e.g. *Ferribacterium limneticum*, and *Geobacter metallireducens*, accelerating the rate of both Fe(III) oxide reduction in river sediments and contaminant oxidation coupled to Fe(III)-reduction (Lovley *et al.* 1996; Finneran and Lovley 2000; Nevin and Lovley 2000). Other iron reducers such as *Shewanella oneidensis* (Venkateswaran *et al.* 1999), *Paludibaculum fermentans* (Kulichevskaya *et al.* 2014), or *Anaeromyxobacter dehalogenans* (Sanford *et al.* 2002) are able to utilize a number of different electron donors including sugars and long chain fatty acids. The broad variety of electron acceptors and donors in iron reducers makes them ubiquitous in freshwater sediments.

In sediments, pyrite (FeS<sub>2</sub>) is oxidized abiotically at mineral surfaces, for example of FeS<sub>2</sub> and MnO<sub>2</sub> (Table 4; Schipper and Jørgensen 2001). Immediate products of this oxidation are thiosulfate and polythionates, which can be further oxidized to sulfate by manganese-reducing



bacteria (Jørgensen and Nelson 2004). In addition, black sulfides in anoxic zones, Fe(II) and Mn(II) were released from sediment pore waters to form black oxides in anoxic-oxic water interface of the black rivers (Atkinson *et al.* 2007). Small amounts of dissolved ferrous iron coming from FeS<sub>2</sub> in sediments can be re-oxidized by oxygen, NO<sub>3</sub><sup>-</sup> and MnO<sub>2</sub> and precipitated as black magnetite in river beds. After reentry in oxic zones or through mediation reduced Mn(II) is recycled to MnO<sub>2</sub> via microbial oxidation in presence of, even trace amount of, O<sub>2</sub> or nitrate in surface waters (Boogerd and de Vrind 1987; Marcus *et al.* 2017). Nitrate has therefore been suggested as cost-effective remediation method for black urban rivers (He *et al.* 2017).

## **Odorous volatile compounds**

### ***Sulfur compounds***

Odorous compounds in urban rivers are volatile organic and inorganic compounds. Volatile sulfur compounds generated from microbial sulfate reduction or degradation of sulfur-containing organic matter normally have unpleasant odor, including inorganic H<sub>2</sub>S and organic sulfides (Kadota and Ishida 2003). Sources of such reduced sulfur compounds vary. River deltas discharging into oceans often experience seawater influx due to tidal activities. Therefore, sulfide, as a result of microbial sulfate reduction, is detected in significant amounts in urban rivers connecting to major deltas in coastal areas, particularly in the Pearl River estuary where 3 mM sulfide in the sediment was reported as a result of sulfate reduction (Fang and Zhang 2005). Most sulfide in estuaries is produced by sulfate reducing microorganisms (SRM) using dissimilatory sulfate

reduction for respiration to generate sulfide. SRM are broadly dispersed across the prokaryotic phylogenetic tree but are often found among *δ-Proteobacteria* and *Firmicutes* as well as *Archaea* (Zhou *et al.* 2011). In addition to production of the odorous H<sub>2</sub>S, sulfate reduction may eventually lead to formation of black iron sulfide species even with trace amounts of iron in the water and sediment (Wu *et al.* 2016).

Another source of sulfide in urban rivers is organic sulfur (Giordano *et al.* 2005). It enters the sulfur cycle via assimilatory sulfate reduction (Fig. 2). The amount of sulfur in domestic waste streams or other anthropogenic sources, however, is negligible compared with the massive cyanobacterial blooms in the surface waters (Zhang *et al.* 2010). CO<sub>2</sub>-fixing cyanobacteria frequently are the main source of organic matter in surface waters. They assimilate sulfur via cysteine-/methionine-biosynthetic pathways (Fig. 2). This organic sulfur is subsequently released in form of volatile organic sulfur compounds (VOSCs), which includes thiols/thioethers in methylated sulfide species, e.g. methyl sulfide, dimethyl sulfide and dimethyl disulfide, as byproducts – all of which are characterized by their notoriously bad smell (Bentley and Chasteen 2004).

### ***Nitrogen and organic carbon compounds***

Nitrogen compounds are the largest group of malodorous compounds generated by proteolytic microorganisms, and their smells range from ammonia to the typical smell of corpse decomposition (Wang *et al.* 2017). Microbiogenic malodorous nitrogen compounds include organic amines such as cadaverine (1,5-pentanediamine) and putrescine (1,4-butanediamine). Cadaverine is produced via decarboxylation of lysine, whereas putrescine is a product of ornithine degradation, an essential building block of bacterial cell walls (Wunderlichová *et al.* 2014; Ma *et al.*

2017). Other abundant malodorous nitrogen compounds are volatile alkylated amines of characteristic fishy smell, which is sensed even in trace amounts. These compounds comprise methylamines, such as methylamine, dimethylamine, trimethylamine, ethaneamine, propaneamine, butaneamine, etc (Ge *et al.* 2011). Methylamines are degradation products of N-methylated amino acids, with glycine, betaine, choline, trimethylamine, and carnitine as their natural precursors in biomass, which, in turn, is introduced into urban rivers via wastewater or algal blooms (Ikawa and Taylor 1973).

All organisms are able to hydrolyze proteins using proteases as this is an essential part of metabolism. Cell internal proteolysis is necessary in every organism, for example to tune its enzymatic machinery to novel environmental conditions or to control vital cell functions.

Microorganisms specifically feeding on peptides can be isolated using Casamino Acids and Trypticase Peptone media, and often yield strains closely related to *Clostridium* species when grown anaerobically. Such proteolytic microorganisms are ubiquitous in anaerobic and aerobic environments alike. Examples for anaerobic environments are rumens (Blackburn and Hobson 1962), anaerobic digesters (Abendroth *et al.* 2015), peat bogs (Juottonen *et al.* 2005), and rice paddies (Weber *et al.* 2001). Typical aerobic environments are many processed food products such as cabbage (Borla *et al.* 2010) and dairy products (Frazier and Rupp 1931). Despite the presence of proteolytic microorganisms, none of the mentioned environments are known for their obnoxious smell. The reason is that protein concentrations are either relatively low or, in case of food products, aerobic conditions prevail. When oxygen is absent, alkylated amines cannot be further oxidized and serve as substrates for sulfate

reducers or methanogens (Lovley and Klug 1983). However, since alkylated amines are gaseous or at least volatile, they often escape before slow growing anaerobic microorganisms are able to degrade them, causing the typical smell in surface waters.

Odorous organic compounds without S and N elements are mostly VFAs, which are generated from anaerobic fermentation of organic pollutants in the waste streams or of decomposed compounds produced by algal blooms (Verstraete *et al.* 1996; Pham *et al.* 2012). VFAs in urban rivers play critical roles in coupling organic carbon compounds with iron- and sulfur-cycles in the surface water (Fig. 3). For example, when sulfate is present, VFAs can be further used as electron donors by sulfate reducing microorganisms and produce malodorous sulfide (Hao *et al.* 2009).

## **MICROBIAL ECOLOGY OF PRISTINE AND POLLUTED FRESHWATER ENVIRONMENTS**

Urban river pollution affects microbial communities in water and sediments with measurable effects on short (Schöll and Szövényi 2011) and long term (Ibekwe *et al.* 2016; Lu *et al.* 2017). This makes microbial community analysis an additional monitoring tool for water quality (García-Armisen *et al.* 2014; Drury *et al.* 2013; Li *et al.* 2016; Köchling *et al.* 2017; Xie *et al.* 2016). Diversity (Drury *et al.* 2013; Staley *et al.* 2013), richness (Lin *et al.* 2014) and variability (Lu, Chen and Zheng 2017) of microbial communities have been affected by anthropogenic pollutants. As expected, coliform growth is correlated with fecal anthropogenic contamination, for example in large streams such as the Danube

River (Hoch *et al.* 1996; Kirschner *et al.* 2009), the Mississippi (Staley *et al.* 2013), as well as smaller rivers such as Jaboatão River in Brazil (Köchling *et al.* 2017), the Reno River in Italy (Ferronato *et al.* 2013), and small creeks of a California watershed (Ibekwe, *et al.* 2016). A clear impact of treated wastewater on community composition and metabolism was reported for the Taif River in Saudi Arabia, where pristine samples showed a higher representation of carbohydrate metabolic genes along with fatty and amino acid anabolic genes as opposed to samples impacted by wastewater (Li *et al.* 2016). The latter were enriched in genes associated with nitrogen and sulfur metabolism, as it would be expected in nutrient rich environments. Inverse metabolic patterns were reported for river sediments in China where energy, carbohydrate, and amino acid related genes were enriched or equal to pristine control sediments (Lu *et al.* 2017).

Algal growth is often considered to be linked to anthropogenic contamination in freshwater systems such as Taihu Lake in China (Huang *et al.* 2017) or the Zenne River in Belgium (García-Armisen *et al.* 2014). However, the mechanisms by which pollution and algal growth are connected are not always clear. For example, Huang *et al.* (2017) found that phosphate as well as organic matter concentration were correlated with cyanobacterial growth in Taihu Lake, whereas in the Danube River, Kirschner *et al.* (2009) identified only a link to organic matter but not any of the other factors investigated, such as phosphate, nitrogen, temperature, etc. This suggests that cyanobacteria live heterotrophically or that bioavailability of inorganic nutrients, or more complex interactions between heterotrophs and cyanobacteria are responsible for algal blooms.

Despite the DNA sequencing revolution of the recent years, it is not clear which factors shape river sediment communities. Some recent

attempts indicate that, indeed, organic matter released into urban rivers by sewage streams promotes growth of certain microbial lineages such as *Acinetobacter*, *Flaviobacterium*, *Thauera*, and *Rhodococcus* in the Zenne River flowing through the Brussels metropolitan area (García-Armisen *et al.* 2014). A similar correlation between organic matter and *Cyanobacteria* was linked to fecal coliforms and *Enterococci* in the Danube (Kirschner *et al.* 2009). The dependence of fecal coliforms on environmental factors, however, was stronger in the water column than in the sediments studied in selected creeks of a southern California watershed (Ibekwe *et al.* 2016). In the Rhône River prodelta microbial variation could be explained by organic matter as well (Fagervold, *et al.* 2014). In addition to organic matter, Ji *et al.* (2016) found that also iron and sulfate concentrations as well as pH were associated with methanogenic networks identified in Amazonian lake sediments.

The pioneering works of Zwart *et al.* (2002) and Newton *et al.* (2011) identified an appreciable bacterial diversity in freshwater systems showing that river and lake communities are similar. In addition, our own comparison of published 16S rRNA gene-sequencing data of 3 Chinese lakes, 2 rivers and one reservoir from three distant areas shows that geographical location best explained the differences between the investigated freshwater environments (Fig. 3). Though contaminated and pristine sites which are in same region cluster closely, but microbial communities still have little difference that may be shown in the microbial populations. *Proteobacteria* are the largest phylum in the prokaryotic tree of life and are therefore also highly abundant in river sediments – polluted or not. Nearly all river and lake sediments surveyed harbored  $\alpha$ -,  $\beta$ -,  $\gamma$ -*Proteobacteria*. The most prominent representative of freshwater  $\alpha$ -*Proteobacteria* is the SAR11 clade (*Pelagibacter*; Salcher *et al.* 2011;

Savio *et al.* 2015). Also *Bacteroidetes* were found in nearly all freshwater sediments. Together, these four groups cover 40% of all cultured prokaryotic species, making their dominance in freshwater sediments only natural. Consequently, microbial communities in freshwater sediments are often very similar on phylum level (Ji *et al.* 2016). Nonetheless, a study screening 68 publications of lake microbial communities using only high quality Sanger-sequencing data reported a large heterogeneity on lower taxonomic levels, termed tribes (Newton *et al.* 2011). This finding was confirmed for Mississippi River sediments where only 12% of the identified operational taxonomic units (>97% sequence identity) were shared across all sites (Staley *et al.* 2013). It is hence the less abundant groups, such as *Acidobacteria*, *Actinobacteria*, *Verrucomicrobia*, *Chloroflexi*, *Planctomycetes*, *Gemmatimonadetes*, *Archaea*, etc. or tribes that may act as distinctive indicators for metabolic processes. Many such tribes are uncultured representatives of freshwater environments and do not match with Linnaean taxonomic boundaries. While broad surveys of our drinking water resources need to be continued, it remains unclear how underrepresented parts of microbial communities adapt to pollution. Indeed, a recent metagenomic survey of a wastewater impacted river showed that small community factions are major hubs in microbial assemblages (Li *et al.* 2016). An observation that has also been made in the pristine Lake Cadagno, Switzerland, where 0.3% of the cells in the lake were responsible for 40% of the substrate turnover (Musat *et al.* 2008). In conclusion, more studies on natural environments are necessary to understand the above mentioned discrepancies and to establish a baseline for future research on pollution affected environments.

## A SCENARIO OF THE BIOGEOCHEMICAL PROCESS IN BLACKENING AND ODORIZAITON OF URBAN RIVERS

As shown in the scenario depicted in Fig. 4, organic matter originated either directly from anthropogenic sources, e.g. waste streams and other nonpoint source pollution, or from decomposition of cyanobacteria biomass. These are the main suspects in generating odors by producing volatile (organic) sulfides, smelly amines and VFAs (Van *et al.* 1987; Ginzburg *et al.* 1998; Hu *et al.* 2007; Zhang *et al.* 2010). Organic matter is also the major source of reducing equivalents for the reduction of  $\text{SO}_4^{2-}$  and Fe(III) to produce blackening minerals such as iron sulfides which link the sulfur and iron cycles in urban rivers (Fig. 4; Berner *et al.* 1985; Lovley 1987). Therefore, input of organic matters into urban rivers is likely the key factor to trigger the water blackening and odorization. Sulfur input from sediment, seawater, or decomposing algal biomass, is directly involved in the formation of black- and odorous-matters in urban rivers, e.g. via formation of sulfide species such as  $\text{H}_2\text{S}$ , and iron sulfides. Alkylated sulfides are often byproducts of cyanobacterial metabolism and biomass degradation and their volatility makes them strong odorous constituents of some urban rivers' stench. Sulfate reduction by diverse SRMs dominates in sediments because their redox potential confers growth advantages to SRMs over their competitors. For example, the standard redox potential of sulfate reduction ( $-217 \text{ mV}$ ) is slightly more positive than that of hydrogenotropic methanogenic process ( $-240 \text{ mV}$ ). This and the higher energy gain compared with iron reduction suggest that sulfur is the link between the different element cycles as shown for Black Sea sediments (Siegert *et al.* 2013).



## CONCLUSIONS AND FUTURE PERSPECTIVES

The blackening and odorization of urban rivers is a complex bio-geochemical process involving five key elements, i.e. Fe, Mn, S, N, and C.

Outstanding questions include:

1. While we propose several mechanisms that contribute to blackening and odorization of urban rivers like organic matter degradation and metal precipitation, there is no evidence yet that these are indeed the driving factors. In the past, measures to encounter river pollution were taken, such as widespread treatment of industrial wastewater in the Pearl River Delta, sediment removal, etc. Yet, they only mitigated the problem for a short time. Evidence for our hypothesized mechanisms needs to be collected in order to take targeted action. Gathering this evidence requires application of standard tests to assess water quality (listed in Table 5) along with novel molecular techniques and may involve the development of new methods that are more efficient. As shown in this review, the suspected blackening elements (metal sulfides) and three odor-forming elements (S/N/C) should be first targets for water quality analysis investigating blackening and odor formation in the urban rivers.
2. What, if any, are the core microbial communities taxonomically and physiologically, mediating biogeochemical transfers of the key elements in black-odorous urban rivers? Despite the progress in studies on metabolism and element cycles in surface waters, many puzzles exist. For example, the discrepancy in some reports and our own investigations showing that pollution sometimes does and sometimes does not affect

microbial communities. Understanding the core communities coupling all these element cycles in black-odorous urban rivers. Current meta-omic technologies may help to provide in-depth insights.

3. What is the role of minor elements, e.g. Cu, Zn, etc. in the blackening and odorization of urban rivers? Hitherto, very few studies investigated their contribution to the blackening and odorization in surface waters. Whether these trace elements play critical roles in connecting the Fe/Mn/S/N/C cycles warrant future investigation.
4. New water quality standards to address blackening and odorous surface waters need to be developed in China. Current guidelines are insufficient, mostly because it is not clear what the reasons for blackening and odorization are. Defining baselines will be essential to develop standards. Understanding the pathways involved in blackening and malodor generating metabolisms is key to control these processes and develop environmental friendly microbial technologies. For example, scaling microbial fuel cell technology to use the reduced environment of polluted rivers for power production can be an environmentally friendly alternative to current treatment strategies (Ewing *et al.* 2014). Using microbial inhibitor to blocking microbe participate in Fe/Mn/S/N/C cycles.

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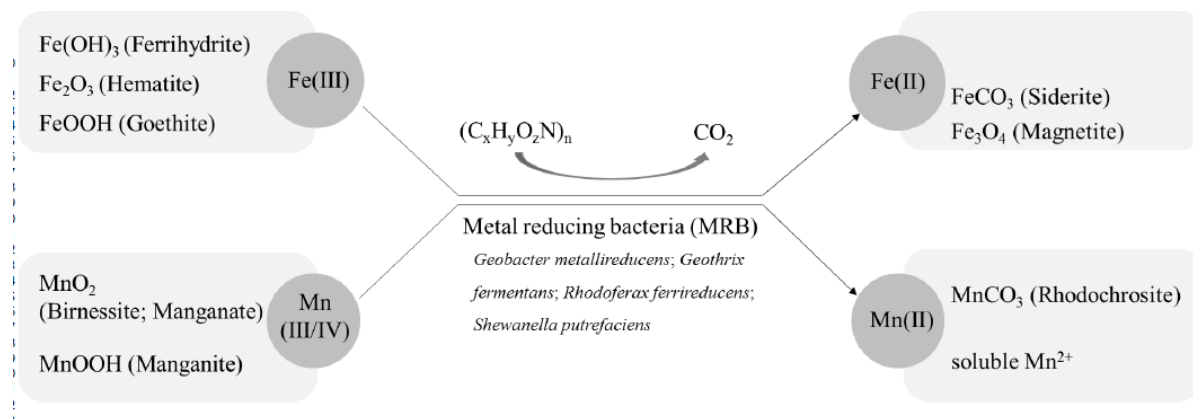
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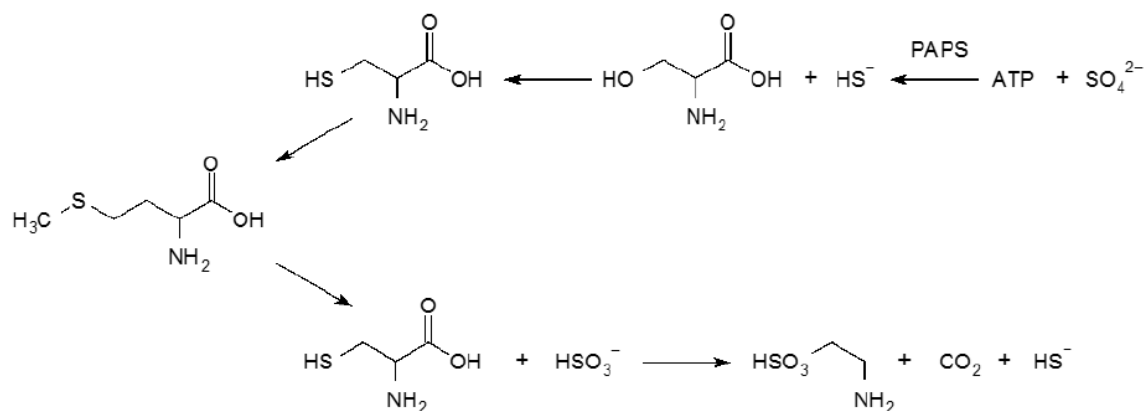
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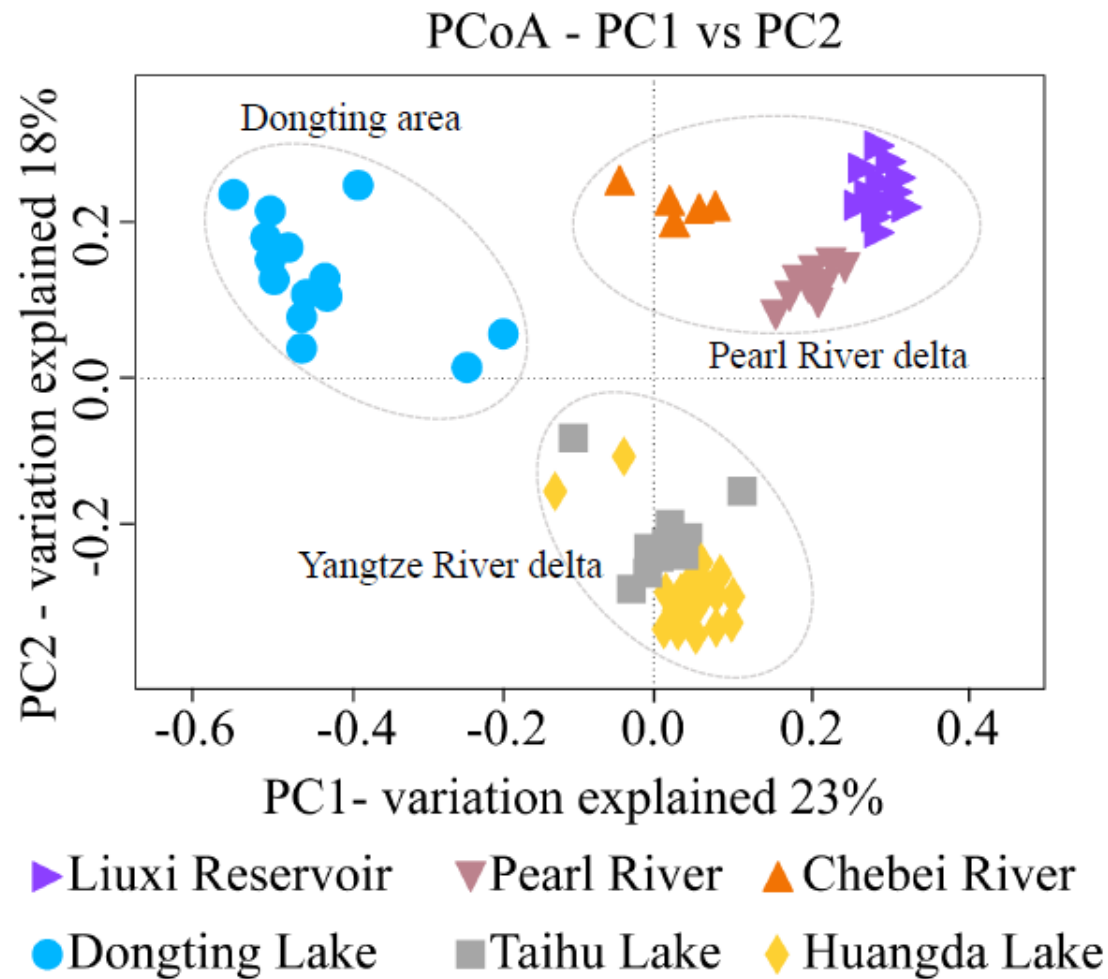
## Figure Legends



**Figure 1.** The microbial mediated reduction of Fe/Mn-minerals in urban rivers

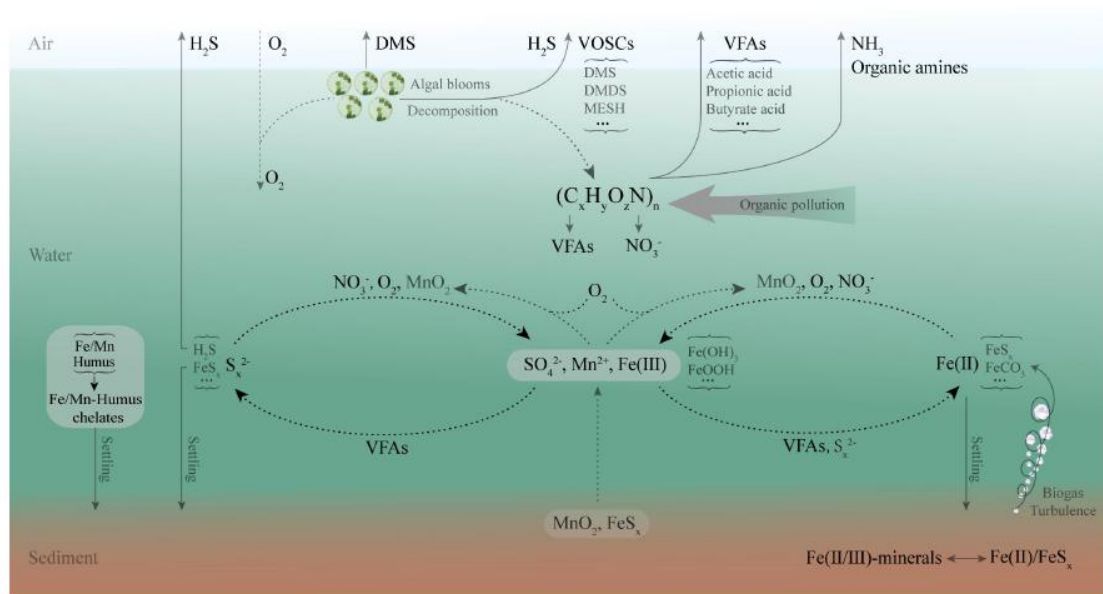


**Figure 2.** Methionine biosynthesis (top) and degradation (bottom) proceed via cysteine. The biosynthetic pathway requires ATP for sulfate reduction to sulfide, producing the intermediate 3'-phosphoadenosine-5'-phosphosulfate (PAPS). Together with serine, sulfide then forms cysteine and ultimately methionine. Under anaerobic conditions, methionine is degraded to taurine, CO<sub>2</sub> and sulfide in exchange for sulfite.



**Figure 3.** Principal coordinate analysis (PCoA with bray-curtis distance matrices) of six surface-water sediment samples collected from three different geographic areas, i.e. Pearl River delta, Yangtze River delta and Dongting area. This figure is plotted with published 16S rRNA gene-

sequencing data (Wang *et al* 2012; Liu *et al* 2014; He *et al* 2017; Huang *et al* 2017). The trophic states of the six surface waters are: eutrophic for Taihu Lake and Chebei River (black-odorous river); mesotrophic for Dongting Lake, Huangda Lake and Pearl River; and oligotrophic for Liuxi Reservoir.



**Figure 4.** Scenarios describing biogeochemical transfers of major black and odorous elements/compounds in urban rivers. In the process of organic matter degraded, odors by producing volatile organic sulfur compounds, methylamines and VFAs generate and escapes into atmosphere.



In addition, organic matter supplying reducing powers for  $\text{SO}_4^{2-}$  and Fe (III) to form  $\text{FeS}_x$ . The processes of black/odorous compounds were marked in solid line, and others in dash line. DMS, dimethyl sulfide; VOSCs, volatile organic sulfur compounds; VFAs, volatile organic sulfur compounds.

## Table Legends

**Table 1.** Differences between organic matter in soil and surface water

Soil			Surface Water		
Soil type	SOM content (%)	Humus (%)	Source	DOC (mg/L)	Humus (mg/L)
Histosols	>80%	32%-60%	Sea water	0.2-2.0	0.06-0.6
Most mineral soils	<5%	<3%	River	1.0-10	0.5-4.0
Tropical soils	2%	0.8%-1.2%	Lake	1-50	0.5-40

SOM, soil organic matter. DOC, dissolved organic carbon.

Sources: Thurman *et al.* 1985; Stanley *et al.* 2000; Juo and Franzluebbers 2003; He *et al.* 2010; Zhang *et al.* 2012; Osman *et al.* 2013; Tfaily *et al.* 2017.

**Table 2.** The content of main elements in crust, soil, surface sediment and surface water

Elements	Crust (%)	Soil (%)	Surface sediments (%)	Surface water(ppm)
O	46-49.52	49		
Si	25.75-27	33		
Al	7.51-8.3	7.1	6.72	0.72084
Fe	4.7-5.8	4	2.61	0.80041
Ca	3.39-5.2	1.5	1.2	
K	2.3-2.64	1.4	2.46	
Na	1.7-2.4	0.15	2.39	
Mg	1.87-2.8	0.5	1.24	6.158
Ti	0.45-0.64	0.5	0.3186	
Cl	0.13-0.19	0.01		
P	0.093-0.12	0.08	0.05485	
C	0.02-0.087	2		
Mn	0.08-0.1	0.1	0.06239	0.01697
S	0.026-0.048	0.07		
N	0.0019-0.003	0.2		
Cr	0.0102-0.03	0.007	0.00997	0.00588
F	0.054-0.0585	0.02		
Ni	0.008-0.0089	0.005	0.00829	0.00188
V	0.009-0.019	0.009	0.00547	
Co	0.0018-0.0025	0.0008	0.00114	0.00045
Cu	0.005-0.006	0.003	0.0108	0.00626
Zn	0.007-0.0094	0.0009	0.0388	0.010943
Pb	0.0012-0.0016	0.0035	0.00547	0.00807
As	0.00018-0.00022	0.0006	0.000885	0.003108
Br	0.00021-0.00025	0.001		

Cd 0.000015-0.00002 3.5E-05 0.0000778 0.00007

Sources: Gaillardet *et al.* 2003; Yang *et al.* 2003; Jefferson 2007; Liu *et al.* 2007; Landaud *et al.* 2008; Viers *et al.* 2009; Feng *et al.* 2010; Lin *et al.* 2012; Song *et al.* 2013; Gao *et al.* 2016; Song *et al.* 2017.

**Table 3.** Major clay minerals composition and content (%) in river sediments

Minerals	Pearl River	Pearl River estuary	Huanghe River	Changjiang River	Changjiang estuary	Molecular formula
Kaolinite	46	40	10	16	10	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Chlorite	25	28	16	12	26	Clinochlore: $(\text{Mg}_5\text{Al})(\text{AlSi}_3)\text{O}_{10}(\text{OH})_8$ Chamosite: $(\text{Fe}_5\text{Al})(\text{AlSi}_3)\text{O}_{10}(\text{OH})_8$ Nimite: $(\text{Ni}_5\text{Al})(\text{AlSi}_3)\text{O}_{10}(\text{OH})_8$ Pennantite: $(\text{Mn},\text{Al})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$
Illite	26	26	62	66	58	$(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$
Smectite	<2	<6	<12	<6	3	Montmorillonite: $(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ Nontronite: $\text{Na}_{0.3}\text{Fe}_2((\text{Si},\text{Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ Saponite: $\text{Ca}_{0.25}(\text{Mg},\text{Fe})_3((\text{Si},\text{Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$
Minor mineral (Pyrite)	<1	<1	—	—	<3	$\text{FeS}_2$

—: Not provided;

Sources: Liu *et al.* 2007; Lu and Wang 1985; Shou *et al.* 2003.

**Table 4.** Thermodynamics of some black or dark metal mineral reactions

Net reaction			$\Delta G^{\circ} / \text{M}$ [kJ mol <sup>-1</sup> ]	$\Delta G^{\circ} / \text{S}$ [kJ mol <sup>-1</sup> ]
Reductive environments				
$\text{SO}_4^{2-} + \text{H}_3\text{C-COO}^- + 3 \text{H}^+ \rightarrow$	$\text{HS}^- + 2 \text{HCO}_3^- + 3 \text{H}^+$		n/a	-48
$\text{Fe}^{2+} + \text{HS}^- + \text{H}^+ \rightarrow$	$\text{FeS}^{\text{a}} + 2 \text{H}^+$		-231	-231
$8 \text{FeOOH}^{\text{b}} + 9 \text{H}_3\text{C-COO}^- + 8 \text{SO}_4^{2-} + 25 \text{H}^+ \rightarrow$	$8 \text{FeS} + 18 \text{HCO}_3^- + 18 \text{H}^+ + 12 \text{H}_2\text{O}$		-93	-93
$2 \text{FeOOH} + 3 \text{HS}^- + 3 \text{H}^+ \rightarrow$	$\text{FeS} + \text{FeS}_2^{\text{c}} + 4 \text{H}_2\text{O}$		-74	-50
$\text{Fe}_3\text{O}_4 + 4 \text{HS}^- + 4 \text{H}^+ \rightarrow$	$2 \text{FeS} + \text{FeS}_2 + 4 \text{H}_2\text{O}$		-61	-46
$\text{FeS} + \text{S}^0 \rightarrow$	$\text{FeS}_2$		-60	-30
$4 \text{FeOOH} + 6 \text{HS}^- + 6 \text{H}^+ \rightarrow$	$\text{FeS}_2 + \text{Fe}_3\text{S}_4^{\text{d}} + 8 \text{H}_2\text{O}$		-57	-38
$2 \text{FeOOH} + 3 \text{HS}^- + 3 \text{H}^+ \rightarrow$	$2 \text{FeS} + \text{S}^0 + 4 \text{H}_2\text{O}$		-45	-30
$\text{Fe}_3\text{O}_4^{\text{e}} + 4 \text{HS}^- + 4 \text{H}^+ \rightarrow$	$\text{Fe}_3\text{S}_4 + 4 \text{H}_2\text{O}$		-38	-28
$9 \text{FeS} + 5 \text{HS}^- + 5 \text{H}^+ \rightarrow$	$3 \text{FeS}_2 + 2 \text{Fe}_3\text{S}_4$		-2	-1
$4 \text{S}^0 + \text{H}_3\text{C-COO}^- + \text{H}^+ + 4 \text{H}_2\text{O} \rightarrow$	$4 \text{HS}^- + 2 \text{HCO}_3^- + 6 \text{H}^+$		n/a	-2
$24 \text{FeOOH}^{\text{a}} + \text{H}_3\text{C-COO}^- + \text{H}^+ \rightarrow$	$8 \text{Fe}_3\text{O}_4 + 2 \text{HCO}_3^- + 2 \text{H}^+ + 12 \text{H}_2\text{O}$		-5	n/a
$8 \text{FeOOH} + \text{H}_3\text{C-COO}^- + 17 \text{H}^+ \rightarrow$	$8 \text{Fe}^{2+} + 2 \text{HCO}_3^- + 2 \text{H}^+ + 12 \text{H}_2\text{O}$		186	n/a
$\text{Ni}^{2+} + \text{HS}^- + \text{H}^+ \rightarrow$	$\text{NiS}^{\text{f}} + 2 \text{H}^+$		-184	-184
$\text{Cu}^{2+} + \text{HS}^- + \text{H}^+ \rightarrow$	$\text{CuS}^{\text{g}} + 2 \text{H}^+$		-171	-171
$\text{CuS} + \text{S}^0 \rightarrow$	$\text{CuS}_2^{\text{h}}$		-33	-16
$\text{Pb}^{2+} + \text{HS}^- + \text{H}^+ \rightarrow$	$\text{PbS}^{\text{i}} + 2 \text{H}^+$		-126	-126
$\text{Zn}^{2+} + \text{HS}^- + \text{H}^+ \rightarrow$	$\text{ZnS}^{\text{j}} + 2 \text{H}^+$		-106	-106
$\text{Mn}^{2+} + \text{HS}^- + \text{H}^+ \rightarrow$	$\text{MnS}^{\text{k}} + 2 \text{H}^+$		-42	-42
$\text{MnS} + \text{S}^0 \rightarrow$	$\text{MnS}_2^{\text{l}}$		167	167
Oxidative Environments			$\Delta G^{\circ} / \text{Fe}$ [kJ mol <sup>-1</sup> ]	$\Delta G^{\circ} / \text{ox}$ [kJ mol <sup>-1</sup> ]

$2 \text{Cr}_2\text{O}_3^{\text{m}} + 3 \text{O}_2 + 4 \text{H}_2\text{O}$	$\rightarrow$	$4 \text{HCrO}_4^- + 4 \text{H}^+$	-1,094	-1,459
$10 \text{FeS} + 6 \text{NO}_3^- + 6 \text{H}^+ + 2 \text{H}_2\text{O}$	$\rightarrow$	$10 \text{FeOOH} + 10 \text{S}^0 + 3 \text{N}_2$	-250	-417
$4 \text{FeS} + 3 \text{O}_2 + 5 \text{H}_2\text{O}$	$\rightarrow$	$4 \text{FeOOH} + 4 \text{S}^0 + 3 \text{H}_2\text{O}$	-270	-359
$\text{HS}^- + \text{MnO}_2^{\text{n}} + 3 \text{H}^+$	$\rightarrow$	$\text{S}^0 + \text{Mn}^{2+} + 2 \text{H}_2\text{O}$	n/a	-130
$2 \text{FeS} + 3 \text{MnO}_2 + 6 \text{H}^+$	$\rightarrow$	$2 \text{FeOOH} + 3 \text{Mn}^{2+} + 2 \text{S}^0 + 2 \text{H}_2\text{O}$	-150	-100
$2 \text{FeS}_2 + 3 \text{MnO}_2 + 6 \text{H}^+$	$\rightarrow$	$2 \text{FeOOH} + 3 \text{Mn}^{2+} + 4 \text{S}^0 + 2 \text{H}_2\text{O}$	-90	-60

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Black or dark minerals are: <sup>a</sup>iron sulfide, <sup>b</sup>goethite, <sup>c</sup>pyrite, <sup>d</sup>greigite, <sup>e</sup>magnetite, <sup>f</sup>millerite, <sup>g</sup>covellite, <sup>h</sup> $\alpha$ -chalcocite, <sup>i</sup>lead sulfide, <sup>j</sup>sphalerite (disulfide not known for Zn and Pb), <sup>k</sup>alabandite (pink, orange or green), <sup>l</sup>hauerite, <sup>m</sup>eskolaite <sup>n</sup>pyrolusite (light grey) the underlined line is the sum of the above reactions; M, metal; n/a, not applicable; ox. oxidant; energies of formation were taken from the CRC Handbook of Chemistry and Physics 89<sup>th</sup> edition, Stumm and Morgan 1996, and E. Westrum and Grønvold 1970.

**Table 5.** Routine methods for surface water quality assessment

Analyte	Method	References
Dissolve inorganic carbon(DIC)	Spectrophotometry/Potentiometry/Conductimetry	Motomizu <i>et al.</i> 1987; Linares <i>et al.</i> 1989; Carlson 1978;
Dissolve organic carbon(DOC)	Chemical oxidation	Sharp 1973
	Ultraviolet oxidation	Beattie <i>et al.</i> 1961; Armstrong <i>et al.</i> 1966
	High-temperature combustion	Sharp 1973; Salonen 1979
Chemical oxygen demand(COD)	Dichromate oxidation method	Moore <i>et al.</i> 1949; Jirka and Carter 1975
	Potassium Permanganate oxidation method	Korenaga 1980;
Metal content (Fe, Mn, Cu, Zn, etc.)	Spectroscopic analysis method (Inductively coupled plasma mass spectrometry, ICP-MS )	Houk <i>et al.</i> 1989
Total dissolve nitrogen(TDN)	Alkaline persulphate digestion	Solorzano and Sharp 1980
	High temperature oxidation	Suzuki <i>et al.</i> 1985
Dissolve inorganic nitrogen(DIN)	Phenol-hypochlorite reaction method ( $\text{NH}_3/\text{NH}_4^+$ )	Bolleter <i>et al.</i> 1961;
	Nessler's reagent spectrophotometry ( $\text{NH}_3/\text{NH}_4^+$ )	Vanselow 1940; Leonard 1963;
	Ion Chromatography ( $\text{NO}_2^-$ , $\text{NO}_3^-$ )	Gjerde <i>et al.</i> 1979
	Colorimetric Method ( $\text{NO}_2^-$ )	APHA Standard Method 4500- $\text{NO}_2^-$ B 1996
	Ultraviolet Spectrophotometric ( $\text{NO}_3^-$ )	Hoather and Rackham 1959
Dissolve organic nitrogen(DON)	High-temperature catalytic oxidation	Badr <i>et al.</i> 2003
Dissolved and precipitated sulfides	CuS colloidal solution method	Cord-Ruwisch 1985
Dissolve sulfate	Turbidimetric method	Tabatabai 1974
Volatile organic sulfur compounds (VOSCs)	Chromatography analysis method (Gas chromatography-sulfur chemiluminescence detector, GC-SCD)	Sun <i>et al.</i> 2014
	Chromatography analysis method (Gas chromatography-mass spectrometer, GC-MS)	Van <i>et al.</i> 1995
Element content(C、H、N、S)	Elemental analyzer	Kirsten 1971; Fadeeva <i>et al.</i> 2008