

**Biogenic Sources of Sulfur Emission to the
Atmosphere and Their On-Site Measurement
Methods**

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Dissertation submitted to the Graduate School
of Science and Technology, Kumamoto University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

September, 2006
Kumamoto, Japan

Dedicated

To

My parents

Abstract:

Biogenic Sources of Sulfur Emission to the Atmosphere and Their On-Site Measurement Methods.

Volatile sulfur compounds (VSCs) are emitted to the atmosphere from both natural and anthropogenic sources. Identification and characterization of sources of atmospheric natural sulfur compounds are essential for the rational formulation of emission control policies design to limit the atmospheric sulfate burden, for analysis of the origins of acidic precipitation, and exploring global climate change. It is a challenge for analytical chemist to analyze VSCs at trace levels in the field because of their highly adsorptive, reactive and volatile properties. In the present research, I have investigated some natural sources of hydrogen sulfide, sulfur dioxide and development of new analytical method for on-site measurement of volatile sulfur gases methyl mercaptan and dimethyl sulfide.

Emission variability of hydrogen sulfide and sulfur dioxide from tidal flat sediments to atmosphere in Ariake Sea, Japan was studied using a diffusion scrubber-based portable instrument. Ariake Sea is a typical closed sea consisting of a huge marsh area along the coast. Seasonal, spatial and diurnal variability in emission rates were examined. In addition, depth profiles of the gas emissions were examined with the profiles of anions, heavy metals, water and organic contents. Unexpectedly, SO₂ emission was much higher than H₂S in all measurements, while an opposite emission trend was observed in diurnal and spatial patterns of H₂S and SO₂ emissions. The mechanisms of these gas emissions are discussed. Total sulfur fluxes to the atmosphere as H₂S and SO₂ during the study averaged 7.1 μgSm⁻² h⁻¹ for muddy sites and 28 μgSm⁻² h⁻¹ for sandy sites. Estimated total sulfur turnover in the whole tidal land of Ariake Sea was 20.2 t S y⁻¹. Sulfur fluxes from tidal flats were comparable to the artificial sulfur emission from the neighboring towns.

Emission of hydrogen sulfide and sulfur dioxide from agricultural soils were studied by using model agricultural field and concentration of these gases in the volcanic gases at Mt. Aso. Emission was investigated from model agricultural field with and without fertilizer. Emission variability also observed with respect to soil physical characteristics. Mean emission rate as SO₂ and H₂S from the four different model fields were 23.98 ± 14.17 and 2.07 ± 3.46 (without fertilizer), 29.39 ± 14.25 and 2.09 ± 4.14 (natural fertilizer), 7.81 ± 5.05 and 2.09 ± 3.98 (chemical fertilizer), 9.02 ± 7.83 and 2.63 ± 4.57 μgS m⁻² h⁻¹ (mixed

fertilizer) obtained. Emission of H₂S was stable during the measurement period. Very high fluctuation of SO₂ emission was observed compare to the emission of H₂S. SO₂ emission was significantly influenced by the soil physical properties e.g. soil moisture content and soil surface temperature. Significant emission was observed from this kind of agricultural field, although, the mechanism of emission is not clear. In active period of volcano, concentration of SO₂ and H₂S were significantly increased. SO₂ concentration was increased up to 15 ppmv whereas H₂S concentration increased up to 1 ppmv.

Simple and automated method for measurement of methyl mercaptan (CH₃SH) and dimethyl sulfide (DMS) has been investigated. These two are the most odorous among the sulfur gases. The collection and subsequently separation are performed with a single short column packed with silica gel adsorbent without any additional separation column. CH₃SH and DMS were separated according to their desorption temperatures and introduced into a chemiluminescence cell in the same order. These two gases were detected based on the strong gas phase chemiluminescence reaction with ozone. Linearity of calibration curves with this system is advantageous compared to flame photometric detector. The total system, including a small cylinder for the carrier nitrogen, can be set in a carriable box. The instrument is applicable to breath odor analysis. Also, automated and continuous measurement of room air could be performed with this instrument. During continuous three days toilet air analysis by the reported instrument, it was observed that the sulfur gases level increased after becoming dark. The sulfur gases in ppbv level were successfully measured without any big interference and complicated experimental procedure. Limit of detection of the method for CH₃SH and DMS was 0.3 and 0.05 ppb respectively.

Acknowledgements

This dissertation could not have been written without **Dr. Kei Toda** who not only served as my supervisor but also encouraged and challenged me throughout my academic program. I owe a great deal to my advisor. I would like to extend my deepest thanks and appreciation to my advisor for his ideas and suggestions for solving obstacles encountered during my research. His supervision and encouragement has helped me to fulfill my goal in graduate research.

I would like to acknowledge my gratefulness to Professor Isao Sanemasa for his instructions and encouragements.

I would like to thank the members of my advisory committee, Professor Masayuki Takamiya, Professor Kimiaki Imafuku and Professor Noriyuki Momoshima for their time and guidance through my graduate study at Kumamoto University.

I am indebted to all of the students of Toda group (both current and former) particularly Dr. Shin-Ichi Ohira for their support, and helpful suggestions during my research work. I really enjoyed their companies.

I would also like to thank Ministry of Education, Sports and Culture, Japan to provide financial support for carrying out this research.

I express my deepest thanks and appreciation to my wife, Nelufa Yesmin, whose moral support was essential for the completion of my studies.

Finally, I would like to express my deepest gratitude to my parents, daughter as well as all of my relatives and well-wishers who have always supported me through all of life's endeavors.

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CHAPTER 1

Introduction to Global Sulfur Cycle

1.1. Introduction and Overview of Global Sulfur Cycle

Sulfur is one of the constituents of many proteins, vitamins and hormones. It recycles like other biogeochemical cycles.

The essential steps of the sulfur cycle are:

- Mineralization of organic sulfur to the inorganic form, hydrogen sulfide: (H_2S).
- Oxidation of sulfide and elemental sulfur (S) and related compounds to sulfate (SO_4^{2-}).
- Reduction of sulfate to sulfide.
- Microbial immobilization of the sulfur compounds and subsequent incorporation into the organic form of sulfur.

Overview: Important reactions of the sulfur cycle

- ✓ *Assimilative sulfate reduction* in which sulfate (SO_4^{2-}) is reduced to organic sulfhydryl groups (R-SH) by plants, fungi and various prokaryotes. The oxidation states of sulfur are +6 in sulfate and -2 in R-SH.
- ✓ *Desulfuration* in which organic molecules containing sulfur can be desulfurated, producing hydrogen sulfide gas (H_2S), oxidation state = -2. Note the similarity to deamination.
- ✓ *Oxidation of hydrogen sulfide* produces elemental sulfur (S^0), oxidation state = 0. This reaction is done by the photosynthetic green and purple sulfur bacteria and some chemolithotrophs.
- ✓ Further *oxidation of elemental sulfur* by sulfur oxidizers produces sulfate.
- ✓ *Dissimilative sulfur reduction* in which elemental sulfur can be reduced to hydrogen sulfide.
- ✓ *Dissimilative sulfate reduction* in which sulfate reducers generate hydrogen sulfide from sulfate.

Reservoirs of sulfur atoms:

- The largest physical reservoir is the Earth's crust wherein sulfur is found in gypsum (CaSO_4) and pyrite (FeS_2).
- The largest reservoir of biological useful sulfur is found in the ocean as sulfate anions (very concentrated at 2.6 g/L), dissolved hydrogen sulfide gas, and elemental sulfur.
- Other reservoirs include:
 - Freshwater - contains sulfate, hydrogen sulfide and elemental sulfur;
 - Land - contains sulfate;
 - Atmosphere - contains sulfur oxide (SO_2) and methane sulfonic acid (CH_3SO_3); volcanic activity releases some hydrogen sulfide into the air.

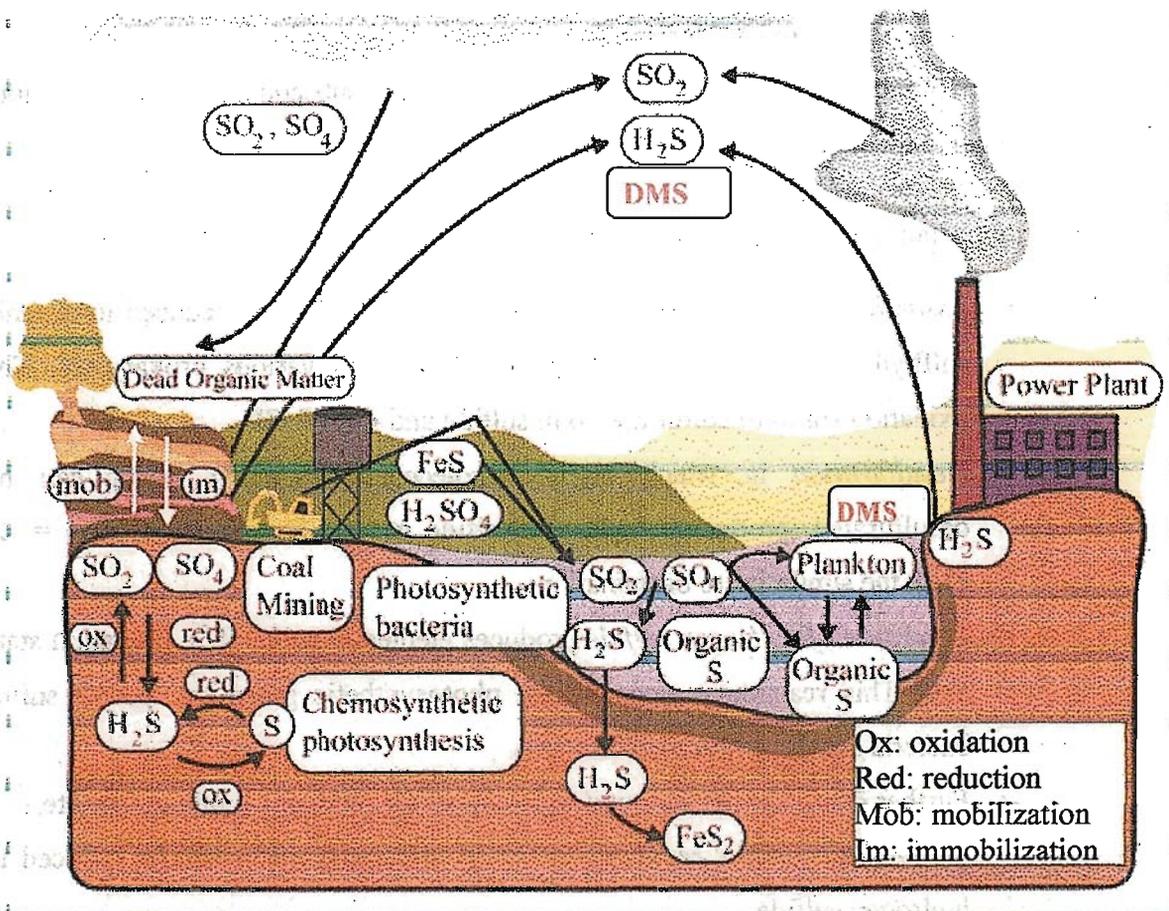


Figure 1.1. Major sulfur transformation in the global sulfur cycle.^{1,2}

Given that Sulfur Is "Already Fixed", Why Bother Studying the Sulfur Cycle?

1. Environmental impacts are diverse and important locally even on a human time scale:

a. Some of the reactions that occur in the sulfur cycle open up new environments to life. They support biological communities in unlikely places such as deep sea thermal vents, areas of low pH and areas of high temperature.

b. On the other hand, certain reactions remove needed metabolites or produce wastes that make environments uninhabitable to some organisms.

2. Interesting microbial chemistries, that no other organisms do, are found in cycles such as the sulfur cycle. They have been exploited in:

a. Mining,

b. Bioremediation,

c. Synthesis of industrial chemicals.

Human impact on the sulfur cycle is primarily in the production of sulfur dioxide (SO₂) from industry (e.g. burning coal) and the internal combustion engine. Sulfur dioxide can precipitate onto surfaces where it can be oxidized to sulfate in the soil (it is also toxic to some plants), reduced to sulfide in the atmosphere, or oxidized to sulfate in the atmosphere through photochemical oxidation as sulfuric acid, a principal component of acid rain.

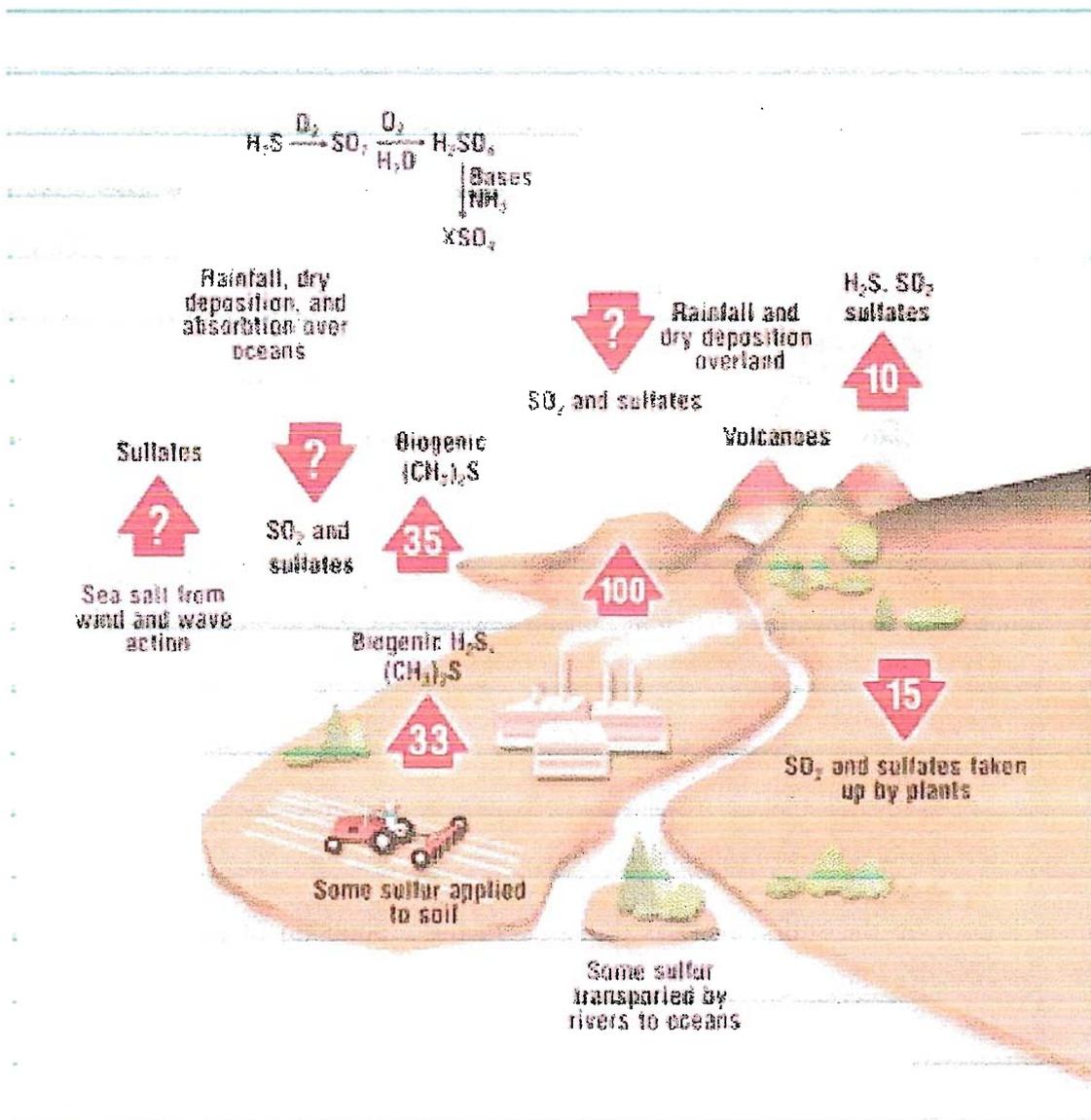


Figure 1.2. Global atmospheric sulfur cycle. Fluxes of sulfur represented by the arrows are in millions metric tons per year. Those marked with a question mark are uncertain, but large, probably of the order of 100 million metric tons per year.

1.2. Sulfur Gases and Their Role in Global Sulfur Cycle

Sulfur-gases in the atmosphere include hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (CH_3SH), dimethyl sulfide (DMS), sulfur dioxide (SO_2) and so on. They play a crucial role in the global sulfur cycle. They are emitted to the atmosphere from natural and anthropogenic sources through a wide variety of complex chemical and biochemical processes and deposited to the earth by wet and dry deposition systems.

1.3. Impact of Atmospheric Sulfur to the Local and Global Environment

It is known that both natural and man-made sources release chemical species that can modify acidic deposition, climate, human health, ecological systems, and visibility. The study of the sulfur cycle has received much attention during recent decades since, apart from its climatic relevance, sulfur via non-sea-salt sulfate is the main contributor to acidity of both wet and dry deposition at urban as well as at remote parts of the world.³⁻⁵

Agriculture, urbanization and releases of various chemical substances into the soil, air and water have altered our environment on local, regional and global scales. In particular, sulfur emissions have grown rapidly and extensive research has documented a variety of effects on the environment. Sulfur emissions play a crucial role in three important environmental problems: local air pollution and smog, acid rain and dry deposition, and global climate change. Not only SO_2 but also reduced sulfur compounds can undergo chemical and photochemical oxidation to yield compounds such as methanesulfonic and sulfuric acid.⁶ Their increases are important because sulfur gases are oxidized in the atmosphere with the formation of sulfate, resulting in environmental problems associated with acid rain. Those sulfur gases may participate and disturb the natural transfer of sulfur of biological origin.^{7,8} It is also evident that sulfur gases play an important role in the formation and growth of aerosol particles in the troposphere: they may alter the optical properties of clouds which may interfere with global climate change.⁹⁻¹¹ Sulfate aerosol may also provide surfaces for heterogeneous reactions that could affect stratospheric ozone levels.^{12,13}

The Intergovernmental Panel on Climate Change (IPCC) report (IPCC, 1994) reconfirmed the ability of aerosols to alter climate by changing the radiative balance of the atmosphere.

In addition, sulfur-containing odorants are subject to strong public criticism.

Consequently, volatile sulfur compounds are important in the atmospheric environment.

1.4. Sources of Sulfur to the Atmosphere

Sulfur in the atmosphere originates either from natural processes or anthropogenic activity.

1.4.1. Anthropogenic Sources

Approximately 100 millions metric tones of sulfur per year enters the global atmosphere through anthropogenic activities, primarily as SO₂ from the combustion of coal and residual fuel oil.³

1.4.2. Natural Sources

Several author reported that natural sources are constitute a large fraction of the atmospheric sulfur burden.¹⁴⁻¹⁶ The major sources of natural sulfur emission are coastal and wetland ecosystems, vegetation, plant and inland soil, oceanic environments, volcanic activity, biomass burning.¹⁷⁻²⁰

1.4.3. Significance of Natural Sulfur Sources to the Global Sulfur Cycle

In biogeochemistry, the sulfur cycle is one of the most complex cycles because oxidation of sulfur varies between - 2 and + 6 and there are a large variety of organic and inorganic species. Large uncertainties remain concerning the chemical species and the magnitude of natural emission of sulfur gases into the atmosphere. Biogenic sulfur that is sulfur compounds which result from biological processes are a vital sources of sulfur to the atmosphere. The annual amounts of sulfur evolved from biogenic sources have been estimated to be 15-50 Tg S yr⁻¹.²¹ Bates *et al.* reported that contribution of natural sources to the global sulfur emission is estimates as 62%.⁵ Identification and characterization of sources of atmospheric natural sulfur compounds are essential for the rational formulation of emission control policies design to limit the atmospheric sulfate burden, for analysis of the origins of acidic precipitation, and exploring global climate change. The significance of the anthropogenic sulfur emissions as well as the climatic importance in the natural sulfur cycle is difficult to assess without first quantifying the sulfur emission from natural sources. Due to this reason, there is a special significance for the investigation on the natural emission of sulfur gases.

1.5. Necessity of Measurement of Natural Sulfur Emission:

Sulfur species emitted from both natural and man-made sources can modify acidic deposition, climate, human health etc. If a controlled reduction in mane-made emissions

were to occur, natural sources would continue to affect acidic deposition, climate, human health and welfare. As a result, the benefits that would be anticipated from such a controlled reduction could be erroneously optimistic if natural sources make a significant contribution to the present total acidic, climatic and atmospheric budget. Therefore, policy decisions regarding possible emission control strategies require, among other inputs, an accurate assessment of the relative importance of natural and man-made sources.

Data on sulfur emissions are important for analyzing and understanding three important environmental problems: local air pollution and smog, acid rain and dry deposition, and global climate change.

In all the early attempts at developing global sulfur budgets, natural emissions were obtained from the amount of sulfur necessary to balance the cycle. This resulted in considerable scatter in the biogenic estimates, from 34 to 267 Tg S yr⁻¹.²² It is possible with the existing data to begin to make estimates of the upper and lower bounds for biogenic emissions based on direct measurements.¹⁹ However, additional data are necessary to assess biogenic sulfur emissions independent of the other portions of the global sulfur cycle.

1.6. Conclusions

To improve the estimation of global natural sulfur emission to the atmosphere, accurate measurement of natural sulfur flux is required. Attempts to estimate natural sulfur emissions have been fraught with both a paucity of data and high natural variability. Moreover, the emissions from plants and inland soils, may play a significant role in global sulfur cycling and very little work has been reported covering this subject. In the present research emission of sulfur gases from natural sources and their on-site measurement method has been investigated.

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CHAPTER 2

On-Site Measurement of Hydrogen Sulfide and Sulfur Dioxide Emission from Tidal Flat Sediment of Ariake Sea, Japan

2.1. Abstract

Emission variability of hydrogen sulfide and sulfur dioxide from tidal flat sediments to atmosphere in Ariake Sea, Japan was studied using a diffusion scrubber-based portable instrument. Ariake Sea is a typical closed sea consisting of a huge marsh area along the coast. Seasonal, spatial and diurnal variability in emission rates were examined. In addition, depth profiles of the gas emissions were examined with the profiles of anions, heavy metals, water and organic contents. Unexpectedly, SO₂ emission was much higher than H₂S in all measurements, while an opposite emission trend was observed in diurnal and spatial patterns of H₂S and SO₂ emissions. The mechanisms of these gas emissions are discussed. Total sulfur fluxes to the atmosphere as H₂S and SO₂ during the study averaged 7.1 μgS m⁻² h⁻¹ for muddy sites and 28 μgS m⁻² h⁻¹ for sandy sites. Sulfur fluxes from tidal flats were comparable to the artificial sulfur emission from the neighboring towns.

2.2. Introduction

Ariake Sea is one of the best-known semi-closed seas in Japan and has unique features. Its tidal area is the largest in Japan. Tidal range at the flood tide is about 3 m in the bay mouth area, and it becomes bigger in the bay head area with the tidal range of 4.5–5 m. Many rivers flow into the eastern coast area of Ariake Sea and carry 440,000 tons of sediments per year. Big grain sediments accumulate in the eastern coast, and minute grains are brought by the residual current and accumulate in the bay head to form vast tidal flats with fine sediments.¹ Rivers load nutrients and organic waste into the tidal flats. On the other hand, seawater supplies sulfate periodically. In these situations, sulfur gases are supposed to emit largely from coastal sediments. However, there has been no quantitative study on biogenic sulfur emission from tidal flats of Ariake Sea. Environmental issues related to Ariake Sea have been a topic of increasing interest recently¹⁻⁵ and analysis of characteristics of tidal flats is of great interest to the regional population.

Reducing sulfur gases, such as hydrogen sulfide (H₂S), methylmercaptan (CH₃SH) and dimethylsulfide (DMS) and so on, involves chemical and photochemical oxidations to yield methanesulfonate and sulfuric acid.⁶ It is recognized that not only sulfur dioxide (SO₂), but

also these reducing sulfur gases contribute largely to the formation and growth of aerosol particles in the troposphere. These aerosols are thought to alter the optical properties and contribute to acid deposition and cloud formation, which may interfere with the global climate change.^{7,8} The increasing interest in studying natural sulfur emission has become important over the last two decades because of its significant role in the global sulfur cycles. Estimations of natural sulfur emissions were reported to be equivalent to anthropogenic emissions,^{9,10} drawing the attention to the contribution of biogenic sources of volatile reduced sulfur compounds to the global sulfur cycles. Several attempts have been made to measure biogenic sulfur gas emissions from European and American soils and coastal marshes.¹¹⁻¹⁷ H₂S and DMS are the dominant gases emitted from coastal marshes.¹⁸ DMS is the dominant gas released from grass and algae, whereas mostly H₂S is emitted from intertidal mud flats.¹⁹ On the other hand, direct emission of SO₂ from marsh sediments has not been discussed in detail. In a recent report, Macdonald *et al.*²⁰ showed that soils have long been recognized as the sink of SO₂ while soils could be a source. They reported SO₂ emission from acid sulfate soils in Australia as an initial field measurement. An interesting issue that is worth investigating is whether SO₂ is emitted or not, directly from normal neutral soils. In the present work, emission of SO₂ was measured together with H₂S, the dominant reduced sulfur gas, in tidal flats of Ariake Sea, Japan. Both H₂S and SO₂ were simultaneously measured on site at the tideland using a portable instrument that was modified for this purpose. Measurement of sulfur gases is generally complicated with analytical methodological difficulties.¹⁰ In most measurements of sulfur gas emission; the sample is collected, preconcentrated into a column, and then purged to be measured by gas chromatography. In this study, the gases were measured directly on site. The method used was easy to conduct and suitable for field measurement.



Figure 2.1. Huge muddy tidal flat generated at the bay head area. Sampling campaign in the huge muddy tidal flat area at Higashiyoka.

2.3. Materials and Methods

2.3.1. Sampling Sites

Ariake Sea's area is 1,700 km², with an extended 96 km of the bay axis, and an average width of 18km as shown in [Figure 2.2](#). Approximately 207 km² of tidal flat area remain: this corresponds to 13% of the sea area. Sediments in Ariake Sea tidal flats range from medium sand to silty mud type. Medium sand, which accounts for approximately 71% of the total tidal flats, is located mainly in the east and south coast areas. The silty mud type (29%) is mainly near the bay head. The major part of the muddy site is flooded only in spring tide. Higashiyoka (33.181N, 130.261E) located in the bay head was chosen as a sampling site. This area is largely affected by Chikugo River (the biggest river in Kyushu Island), Okinohata River and other rivers. Another sampling site was Sumiyoshi (32.701N, 130.581E), in the south area, which has all types of sediments, i.e., silty mud, medium mud and sandy mud, according to the distance from the mouth of the Midorikawa River. The tide

at all of Sumiyoshi sites is diurnal. The campaign has been carried out at Higashiyoka and Sumiyoshi from September 2003 to January 2005.

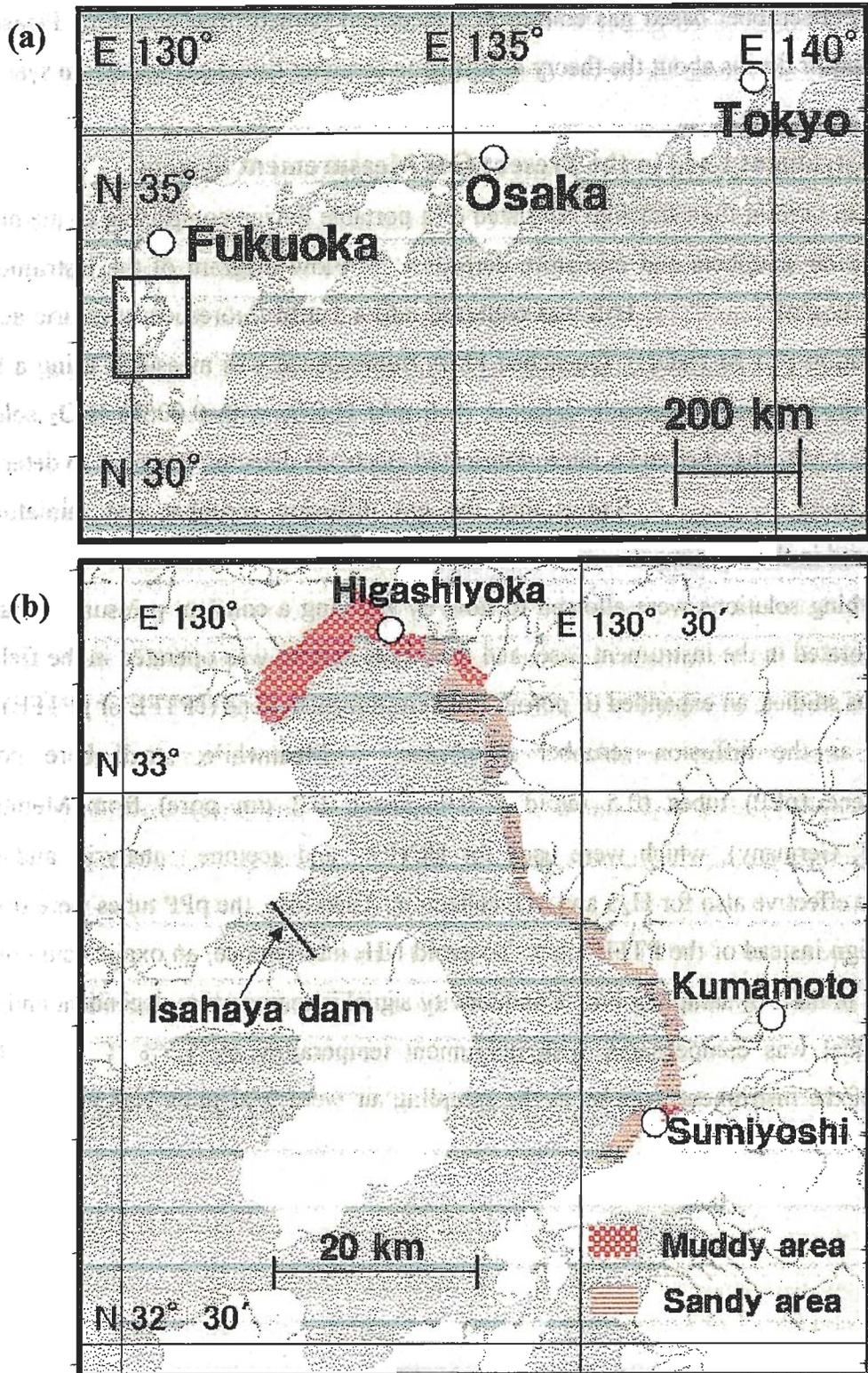


Figure 2.2. Location of Ariake Sea in Kyushu island, Japan (a), sampling sites along the coast of Ariake Sea in the muddy and sandy tidal flat area (b).

2.3.2. Instrument for On-Site Measurement

In the present research we used portable and on-site gas measurement devices comprised with diffusion scrubber based gas collection system and miniaturized detectors. Please see the appendix for details about the theory of diffusion scrubber based gas collection system.

2.3.3. Instrument Used in the Present Gas Measurement System

The system used in the campaign consisted of a portable device comprising of membrane based diffusion scrubbers and miniature detectors.²¹⁻²³ Flow diagram of the instrument is shown in a box of Figure 2.3. H₂S was collected into a 1 mM fluorescein mercuric acetate (FMA) solution (0.1 M NaOH). Quenched FMA fluorescence was measured using a blue-LED/photodiode-based homemade detector. A 5 mM H₂SO₄ with 0.006% H₂O₂ solution was used as a SO₂ absorber and a micro-fabricated electrode detector was used to determine the conductivity. Figure 2.6 Shows that the gas diffusion scrubber and miniaturized detectors used in the instrument.

The absorbing solutions were allowed to flow by applying a constant pressure. A battery was incorporated in the instrument case, and the whole system was operated in the field. In our previous studies, an expanded or porous polytetrafluoroethylene (ePTFE or pPTFE) tube was used as the diffusion scrubber membrane.^{22,23} Meanwhile, small bore porous polypropylene (pPP) tubes (0.5 mmid x 0.9 mmol, 0.2 μm pore) from Membrana (Wuppertal, Germany), which were used for HCHO²⁴ and acetone²³ analysis, and were found more effective also for H₂S and SO₂ collection. Therefore, the pPP tubes were used in this campaign instead of the PTFE tubes. To avoid NH₃ interference, an oxalic acid column was placed in the SO₂ sampling line. Conductivity signal is temperature dependent and span of SO₂ signal was compensated with instrument temperature by 1.5% °C⁻¹. Limits of detection of the instrument in ppbv in the sampling air were 0.02 ppbv H₂S and 0.4 ppbv SO₂.

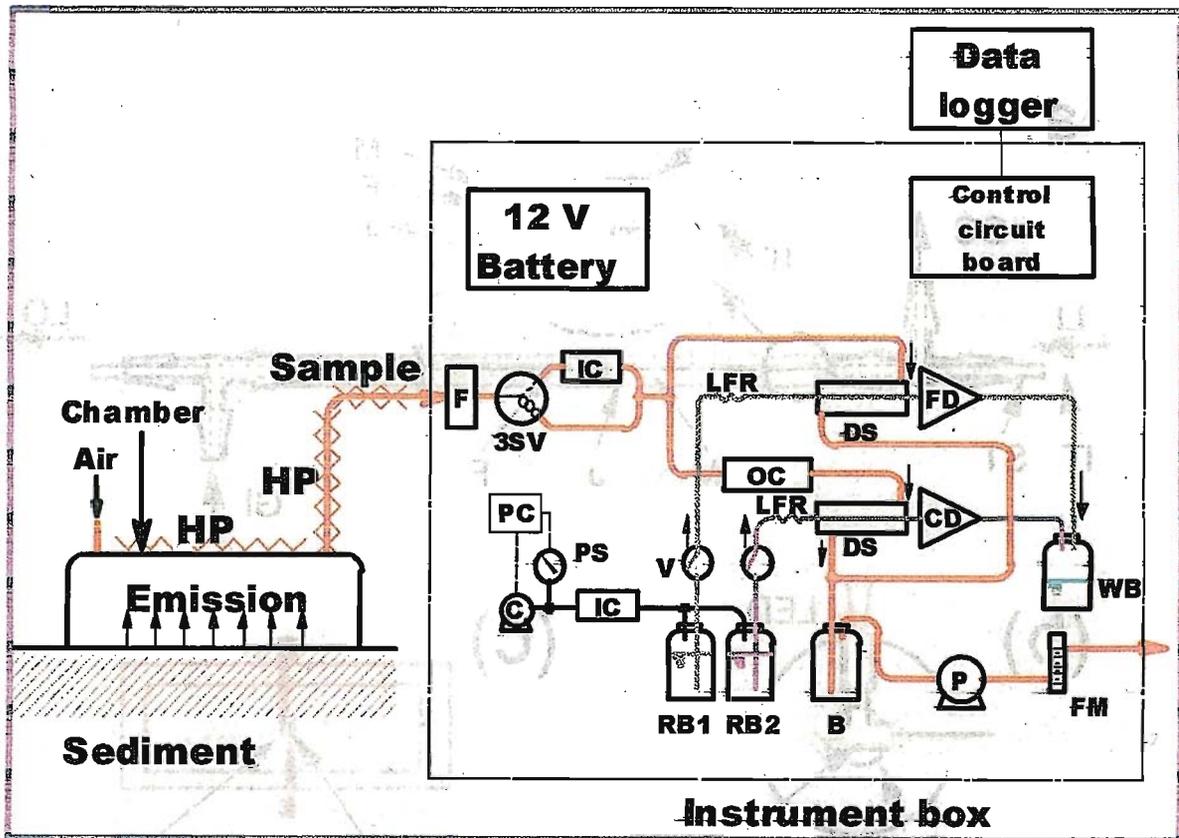


Figure 2.3. Schematic diagram of the sampling/measurement system for simultaneous measurements of H_2S and SO_2 emissions at tidal flats. HP: heating pads, F: inlet filter, 3SV: three-way solenoid valve, IC: iodinated activated charcoal/sodalime column, OC: oxalic acid column, FM: flow meter, B: flow buffer bottle, P: air pump, PC: pressure control circuit, PS: pressure sensor, C: miniature compressor, RB1: FMA reagent bottle, RB2: H_2SO_4/H_2O_2 reagent bottle, V: stop valve, LFR: liquid flow restrictor, FD: fluorescence detector, CD conductivity detector, WB: waste bottle, DS: diffusion scrubber with porous polypropylene tube.

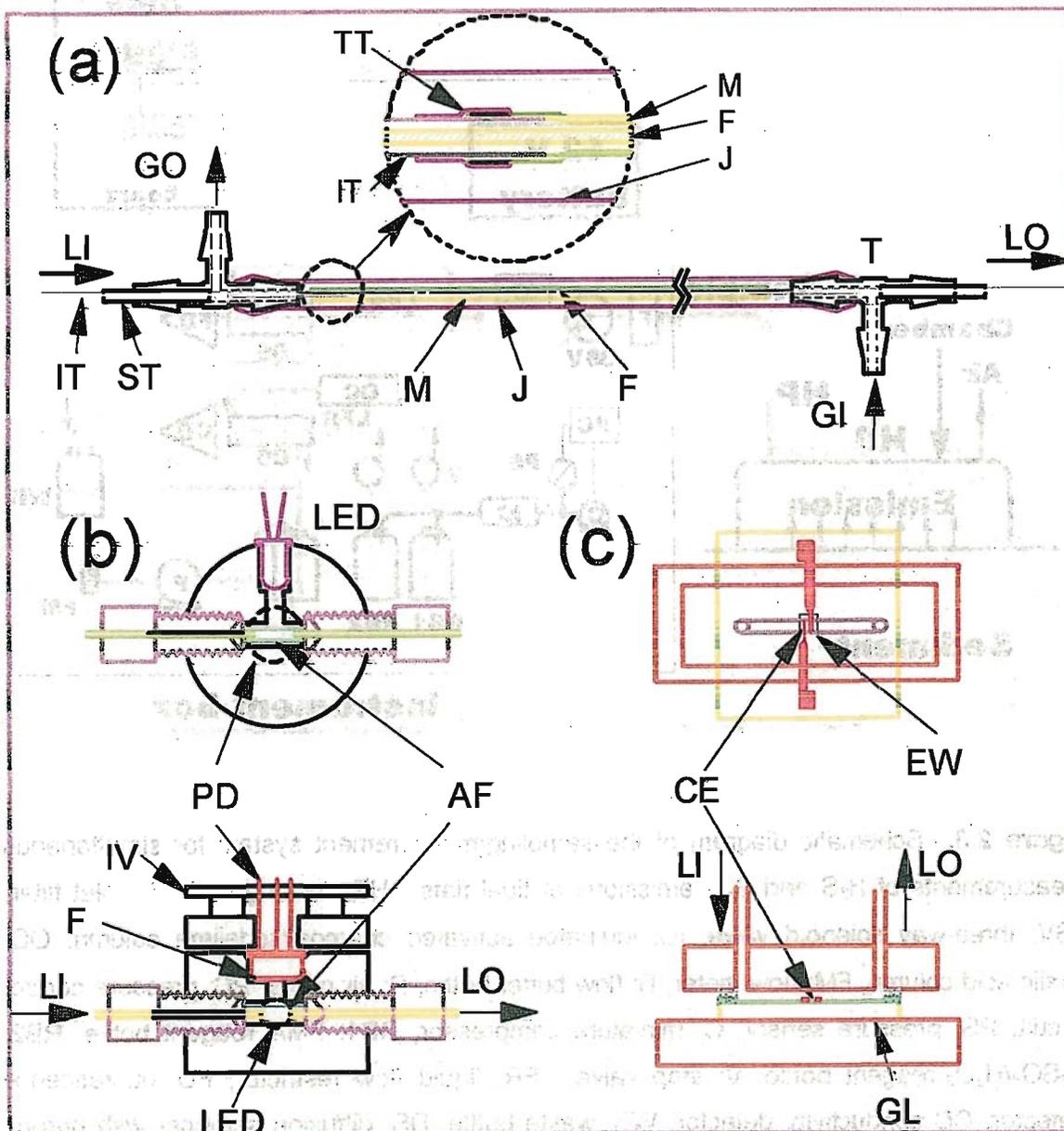


Figure 2.4. Schematic diagram of gas diffusion scrubber and detectors. Parts (a) is structures of scrubber: M, gas permeable membrane tube; J, jacket tube; F, monofilament; T, tee; IT, inserting tube; ST, spacing tube; TT, Teflon tape; LI, liquid inlet; LO, liquid outlet; GI, gas inlet; GO, gas outlet. Parts (b) and (c) are fluorescence detector and conductivity detector, respectively: PD, photodiode; LED, blue LED; F, plastic color filter; AF, Teflon AF tube cell; IV, current-to-voltage converting circuit board; CE, conductivity electrode; EW, electrode window; GL, gasket for liquid flow.

2.3.4. Emission Measurement Procedure at Sediment-Atmosphere Interface

The instrument mentioned above was used for measurement of the gases emitted from the sediment surface. A plastic chamber made of polypropylene was used for sampling as shown in the left of Figure 2.3. The chamber was 21 cm w x 28 cm d x 9.5 cm h (sampling surface area 0.0588 m², volume of the chamber 5.8 l), and had two ports for air inlet and outlet. The chamber was placed on the sediment, and air was aspirated from the air outlet to the instrument via a 1m Teflon tube (3mmid x 6mmod) at a constant flow rate (2.2–2.5 l min⁻¹). In order to prevent water condensation, the tube and the upper part of the chamber were kept warm at approximately 50 °C by using heating pads and wrapping them with a plastic sheet. Heating pads are packed with ferric powder and commonly available for heating at drug stores. Usually, a measurement was conducted for 10 min. and ambient levels of H₂S and SO₂ were 0.2–1.0 ppbv and a few ppbv, respectively, in the campaign field. In the surface measurements, they increased to reach a constant level: H₂S level was usually within 2 ppbv (sometimes near 20 ppbv), and SO₂ was several to 20 ppbv in the sampling air. Emission rates, *E*, in μgS m⁻² h⁻¹ were determined from these increases in the gas concentrations (*DC*, ppbv), the sediment area in the chamber (*A*, m²) and the total air sampling rate (*F*, l min⁻¹ as the standardized flow at 0 °C and 1 atm):

$$E = 32.1 \times 10^6 (\Delta C \times 10^{-9}) (60 F) / 22.4 A \dots \dots \dots (2.19)$$

Usually, the chamber place was changed in the every measurement to avoid increase in temperature by greenhouse effect of the chamber. Temperatures of the sediments, sample air and the instrument inside were monitored simultaneously with platinum temperature sensors. Calibration of the instrument was performed daily before and after the sampling campaign. Zero-signal was checked at least once in 2 h by passing air through a column packed with iodinated activated charcoal/sodalime. The surface measurements were conducted for investigation of spatial variation in the different sediments in Sumiyoshi, seasonal variation at muddy Higashoyoka and sandy Sumiyoshi. Daily variation was examined at typical silty mud sediment in Higashiyoka one time because the repetition of on site measurement overnight was not feasible due to the sampling site being far away from the laboratory and for safety reasons.

2.3.5. Depth Profile Measurement of Soil Gases

Depth profile measurements were performed for the sediment at horizontally 18m from the bank in the muddy tidal flat, Higashiyoka. Sediments (16 kg each) vertically below the surface at 0–2, 10–15, 20–25, 40–45, 60–65, and 80–85 cm depths were sampled into a plastic container (30 cm w x 26 cm d x 16 cm h) and brought back to the bank. The same chamber as the surface measurement was covered onto the sampled sediments, but a sodalime/charcoal column (10mm id x 12 cm L) was placed at the air inlet of the chamber to eliminate gases contained in the outside air. Sulfur gases were strongly emitted by vacuum pressure at 87 ± 7 mm H₂O generated by aspirating air through the column. After emission peaks appeared then the emission gas levels decreased gradually. Amounts of H₂S and SO₂ emitted in 10 min aspirating were measured, and emission in $\mu\text{gS kg}^{-1}$ was obtained from the peak area in the gas concentration vs. time chart, total sampled gas volume and sampled soil weight.

2.3.6. Determination of Physical and Chemical Characteristics of Sediments

At the time of the soil sampling for the gas measurement, fresh sediments were taken into airtight polyethylene bags to examine depth profiles of water and organic contents, distribution of sulfide, sulfate and other anions. Water content and bulk organic matter were determined from decrease in weight after drying at 105 °C for 24 h, and loss-on-ignition of dried samples after 6 h at 520 °C.²⁶ For anion analysis, 10 g wet sediments were homogenized with purified water in a test tube, centrifuged and filtered by used a membrane filter. The filtrate was diluted to be 50 ml, and this was used as a sample solution. 5ml of the sample solution was mixed with 5ml of 20 mM FMA alkaline solution in a test tube, and the fluorescence intensity was measured with a spectrofluorometer (FP-6200, JASCO, Tokyo). Soluble sulfide was determined from the quenching intensity of FMA fluorescence. Other anions were determined by injection of the sample solution into an ion chromatograph IC (761 Compact IC, Metrom, Herisau, Swiss) with an anion separation column (Shodex IC SI-90 4E, 4 mm id x 250 mm long). In case of SO₄²⁻ and Cl⁻ analyze by IC, the sample was diluted 200 times prior to the injection.

2.4. Results and Discussions

2.4.1. Sediments Characteristics of Ariake Sea

Higashiyoka is a typical huge muddy site located in the bay head area with sediment particle size ranged from 5 to 50 mm. Muddy sediments were neutral (pH 7.4) and showed

high water and organic matter contents (62.7 and 4.06%, respectively). We could find a patchy coverage of halophytic plant (*Suaeda japonica mikino*) only by the bank,²⁷ with an abundance of mudskippers (*Boleophthalmus pectinirostris*) and lugworms (*Neanthea japonica*) along the seashore. The other site, Sumiyoshi, was located in the east coast area near the bay mouth, and the sediment type was mainly medium sand but there were partially muddy sand and silt mud. The muddy sand was a transition area, with a 2–5 cm thick coverage of mud and sand mixture and particle size increased with the depth. The muddy sand sediment was observed with abundance of *Scopimera globosa* and bivalves (*Ruditapes philippinarum*).

Table 2.1.
Sediment characteristics of Higashiyoka and Sumiyoshi and mean flux of H₂S and SO₂ to atmosphere from three types of sediment at Sumiyoshi

	Higashiyoka	Sumiyoshi		
	Mud	Mud	Sandy mud	Sand
Particle size (µm)	5 – 50	5 – 50	20 – 200	100 – 400
pH	7.4	8.4 – 8.9	7.4 – 7.6	7.4 – 7.6
Water (%)	62.7	60.7	49.5	25.1
Organic (%)	4.06	4.16	2.26	1.64
General	Patchy coverage of halophytic plants along the bank		No plant	
Gas emission (µgS m ⁻² h ⁻¹)				
n		10	7	10
H ₂ S		8.97 ± 5.5	5.49 ± 4.5	2.43 ± 0.67
		3	9	
SO ₂		4.98 ± 1.30	43.0 ± 7.7	46.1 ± 10.
				7
Total		14.0 ± 5.4	48.5 ± 7.5	48.5 ± 10.
				6

The medium sand sediment was highly water permeable and had low organic matter content as shown in Table 2.1. According to the microscope observation, grain sizes of mud, muddy sand and sand were 5–50, 20–200 and 100–400 mm, respectively. The soil pH of muddy sand and sandy sediments was 7.4–7.6, and muddy sediment pH was 8.4–8.9 at Sumiyoshi.

2.4.2. Spatial Emission Variation

Measurements were performed in April to June 2004 at muddy, sandy muddy and sandy sediments all in Sumiyoshi. Distinct emission variability was observed with respect to spatial change as shown in Table 2.1. The highest mean emission rate of H₂S was at the muddy site ($8.97 \pm 5.53 \mu\text{gS m}^{-2} \text{h}^{-1}$), and the lowest was at the sandy site ($2.43 \pm 0.61 \mu\text{gS m}^{-2} \text{h}^{-1}$); whereas the highest emission rate of SO₂ was at the sandy site ($46.1 \pm 10.7 \mu\text{gS m}^{-2} \text{h}^{-1}$), and the lowest was at the muddy site ($4.98 \pm 1.30 \mu\text{gS m}^{-2} \text{h}^{-1}$). Emission of SO₂ was dominant over H₂S at the sandy and muddy sites during the measurement period. Higher fluxes of SO₂ were found at the site, which sediments were larger in particle size with low-organic matter content, but higher H₂S fluxes were observed on the sediments of smaller particle size containing high-organic matter.

2.4.3. Seasonal Variation of H₂S and SO₂ Fluxes

Emission rates varied with seasonal changes as shown in Figure 2.5 (Note that H₂S bars are enlarged ten times). They were measured in daytime at muddy site Higashiyoka and sandy site Sumiyoshi. At muddy site, the highest H₂S emission was observed in July ($1.1670.19 \mu\text{gS m}^{-2} \text{h}^{-1}$), and the lowest was in September ($0.07 \pm 0.01 \mu\text{gS m}^{-2} \text{h}^{-1}$). Fluxes of H₂S at muddy site were higher in warmer months, except September, than those in cooler months. At the same site, the highest SO₂ emission was measured in September ($10.3 \pm 1.0 \mu\text{gS m}^{-2} \text{h}^{-1}$), and the lowest in October ($1.74 \pm 0.53 \mu\text{gS m}^{-2} \text{h}^{-1}$). Emission of SO₂ did not show any regular trend with seasonal changes at the muddy site. On the other hand, in the sandy site, the highest H₂S flux was observed in June ($0.81 \pm 0.53 \mu\text{gS m}^{-2} \text{h}^{-1}$) and lowest in January ($0.29 \pm 0.07 \mu\text{gS m}^{-2} \text{h}^{-1}$). Emission rate of SO₂ at sandy sites ranged from $3.16 \pm 0.11 \mu\text{gS m}^{-2} \text{h}^{-1}$ (January) to $42.9 \pm 9.4 \mu\text{gS m}^{-2} \text{h}^{-1}$ (June). Apparent emission patterns were observed for both H₂S and SO₂ at sandy sites with seasonal changes. Emission rates of SO₂ were drastically low in winter. The highest emission was observed when the temperature was highest among the measurement campaigns at this site.

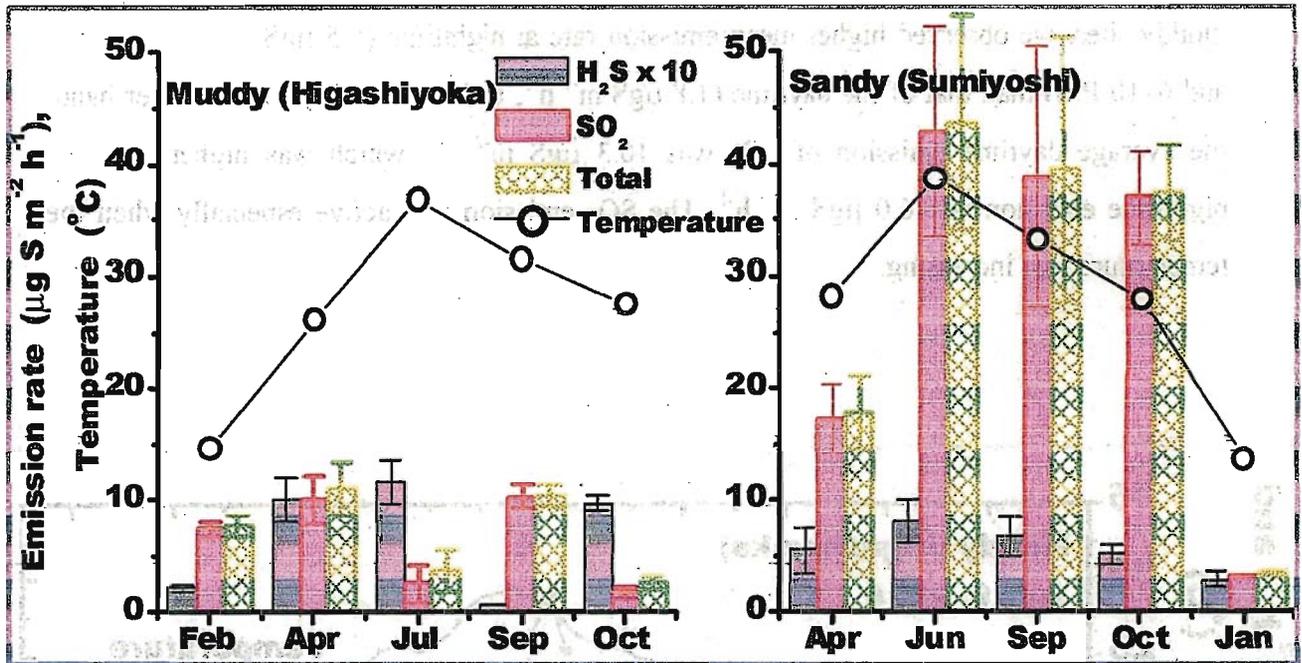


Figure 2.5. Seasonal variations of sulfur fluxes as H₂S and SO₂ from muddy and sandy sites. Measurements were performed during the day at Higashiyoka from February to October, 2004; and at Sumiyoshi from April, 2004 to January, 2005. Note that the bars for H₂S emission are enlarged ten times. In each campaign, the measurements were performed 10 times.

2.4.4. Diurnal Variation of H₂S and SO₂ Fluxes

Diurnal emission was investigated at muddy site Higashiyoka in July 2004. It was at the neap tide, so that seawater did not come to the beach even in high tide time in the bay head area. Figure 2.6 shows diurnal patterns of H₂S and SO₂ emissions and atmospheric temperature. In the diurnal pattern of H₂S emission at the sediment–atmosphere interface of muddy sites, we observed higher mean emission rate at nighttime (5.5 $\mu\text{g S m}^{-2} \text{ h}^{-1}$, 3–6 AM and 6–10 PM) than that of the daytime (1.8 $\mu\text{g S m}^{-2} \text{ h}^{-1}$, 6 AM to 6 PM). On the other hand, the average daytime emission of SO₂ was 10.3 $\mu\text{g S m}^{-2} \text{ h}^{-1}$, which was higher than the nighttime emission rate 6.0 $\mu\text{g S m}^{-2} \text{ h}^{-1}$. The SO₂ emission was active especially when the temperature was increasing.

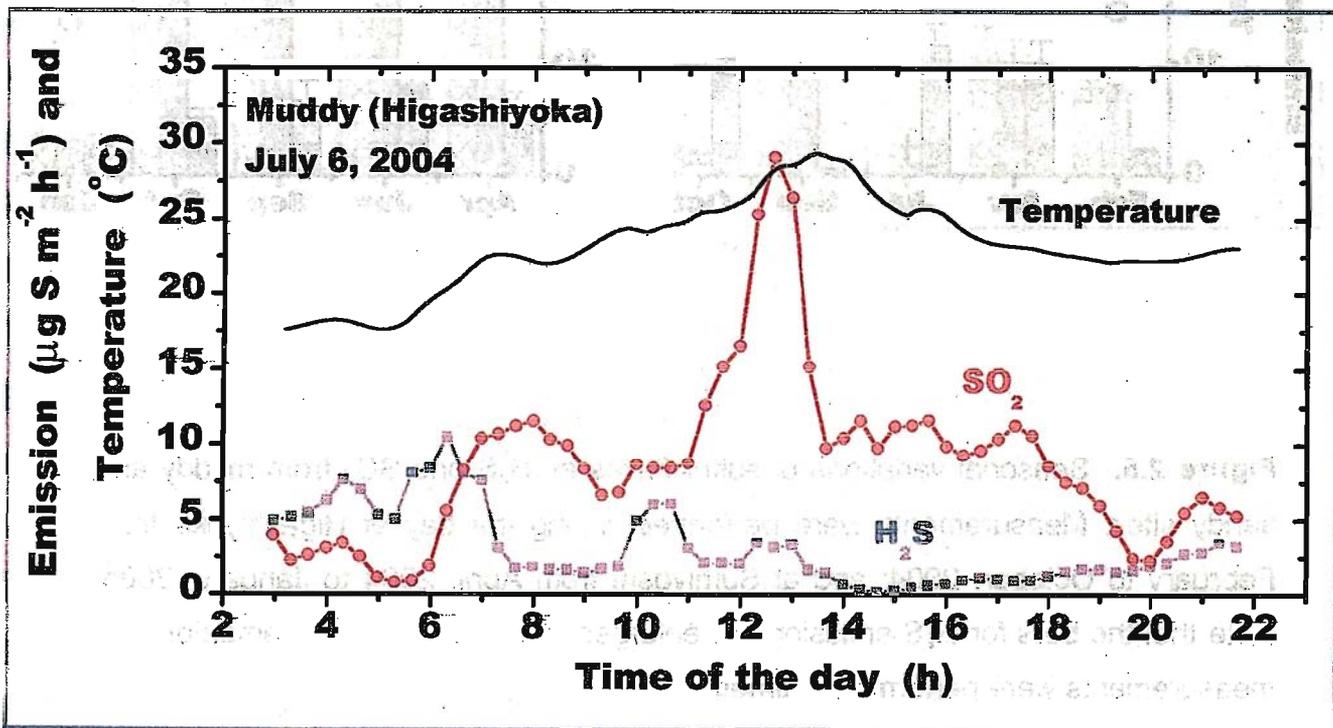


Figure 2.6. Diurnal variations of sulfur flux. Measurement was performed during the neap tide period at muddy site, Higashiyoka in July, 2004.

2.4.5. Vertical Distribution of Active Ions and Gas Emission

Gas contents in the sediments vertically below the surface at the silty mud site (Higashiyoka) were investigated in July, 2004. Results are shown in Figure 2.7 with the vertical distribution of anions, heavy metals and contents of water and organic matter. In these sediments, water content was almost constant from the surface to 80 cm depth. Organic matter obtained from the loss-on-ignition was richer near the surface. Bioactivity was supposed to be higher in the shallow area. Anions from seawater such as Cl^- , SO_4^{2-} and NO_3^- decreased largely with the depth in the first 20 cm. But, only SO_4^{2-} continued to decrease in deeper area while Cl^- and NO_3^- were constant at depths from 20 to 80 cm. This result showed that SO_4^{2-} supply from seawater to the sediment was not sufficient to generate sulfur gases highly, and this helped to explain the low H_2S emission at Higashiyoka as discussed later in the next section. On the other hand, sulfide content was almost constant with the depths but a bit higher in the surface and 40–45 cm. Although change ratios were different but H_2S and sulfide contents showed a similar trend (Figure 2.7 a, b). On the other hand, SO_2 emission peak was around 20 cm in the depth. In the same region, there was a dent in H_2S emission. This region was supposed that the conversion of H_2S to SO_2 was active. The lack in SO_2 emission near the surface might be explained by partial emission of SO_2 before soil sampling. Sediments in the shallow area were rich in sulfur gas sources, such as SO_4^{2-} and organic matters, and effective materials for sulfide oxidation such as NO_3^- and heavy metals.

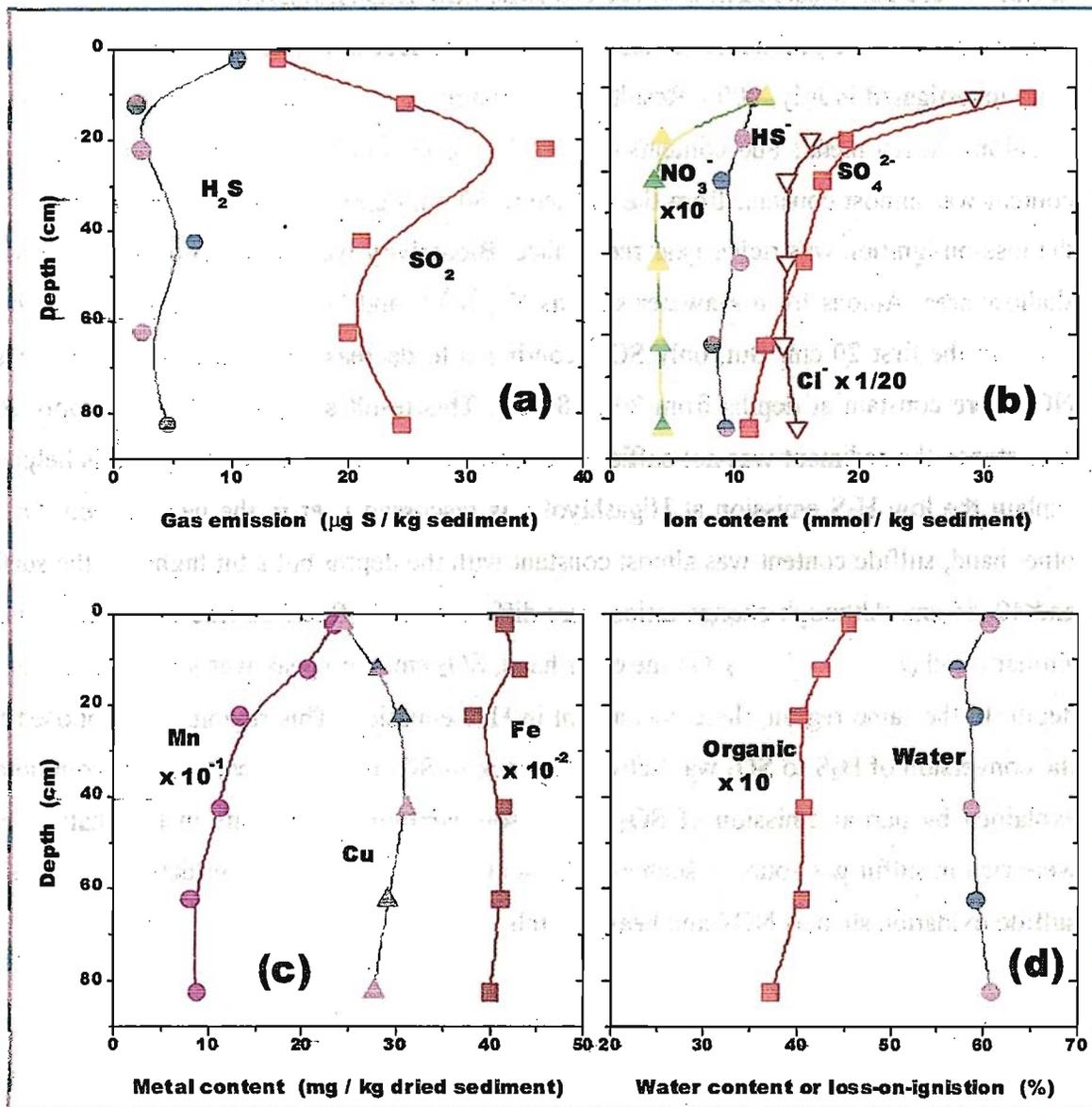


Figure 2.7. Depth profile of (a) gas emissions, (b) ions, (c) metals and (d) organic/water contents. Gas measurement and soil sampling were performed in July 2004 at muddy site, Higashiyoka.

2.4.6. Emission of H_2S

Numerous biological and physical parameters govern sulfur cycling in the coastal wetland. The major sources of reduced sulfur in tidal flat sediments are microbiological sulfate reduction and organic matter decomposition as shown in Figure 2.8. Sulfate is supplied to the sediment from seawater. H_2S is generated in the sediments from sulfate through activity of the sulfate-reducing bacteria. These obligatory anaerobic bacteria oxidize organic compounds and molecular hydrogen by using sulfate as an oxidizing agent.³⁸ In this way, the emission of

H₂S is related to the microbial activity. Hence, higher emission rate was observed at muddy sediments in the warmer seasons.

Seasonal emission patterns obtained at Ariake Sea tideland were similar to the data obtained in Wadden Sea¹⁶ and the estuary of River Colne, UK.²⁹ Summer H₂S emission rates reported are 66.88±1.72 μgS m⁻² h⁻¹ at Wadden Sea, 13.2 μgS m⁻² h⁻¹ at saltpan of River Colne and 2.33±0.81 μgS m⁻² h⁻¹.¹⁷ Our result obtained at Ariake Sea, which was 1.16±0.19 μgS m⁻² h⁻¹ in July at matter was unavailable in our study site. Surface layer of sediments contained 4.56% organic matter (Figure 2.9d). However, the supply of organic matter from seawater to sediment was not achieved everyday, and the remaining organics were supposed to be relatively stable matters. In this way, unavailability of reactive organic matter in the sulfate-reducing zone might also explain the low emission rate.

Oxidation of H₂S might be another reason of low emission rate. Kristensen *et al.*²⁶ found that close coupling between H₂S production near the surface and oxidation by oxygen was the cause of low H₂S emission fraction. Most commonly, H₂S is removed by chemical oxidation in the underlying sub-oxic zone (or NO₃⁻-Mn-Fe zone) and precipitation reactions, which lead to precipitation as FeS and FeS₂.³⁰ The high concentration of Mn and NO₃⁻ near the sediment surface (Figure 2.7c) substantiates the removal of sulfide through oxidation.

In the diurnal emission pattern (Figure 2.6), oxidation of sulfide in the surface sediments might explain the lower H₂S emission in daytime compared to that in nighttime. The diurnal emission pattern was similar to data reported by Bodenbender *et al.*¹⁶ for muddy sediments. They stated that high H₂S emission rate during nighttime indicated a shift in the balance between production and consumption processes. The lack of benthic photosynthesis at night suggested that a reduced O₂-barrier facilitated H₂S transfer from sediments to atmosphere. Sulfide oxidation (ultimately to sulfate) generally accounts for 50 to 100% of the oxygen consumption in marine sediments.^{19,31} In the case where an O₂-H₂S interface exists, sulfide oxidation may proceed rapidly and directly via oxygen notably by colorless sulfur bacteria of the *Beggiatoa* type.³² Reoxidation of H₂S contributes to H₂S removal more than precipitation as pyrites in marine sediments.¹⁶ Interestingly, it is said that 1640–30600 times more H₂S are produced than emitted.²⁶

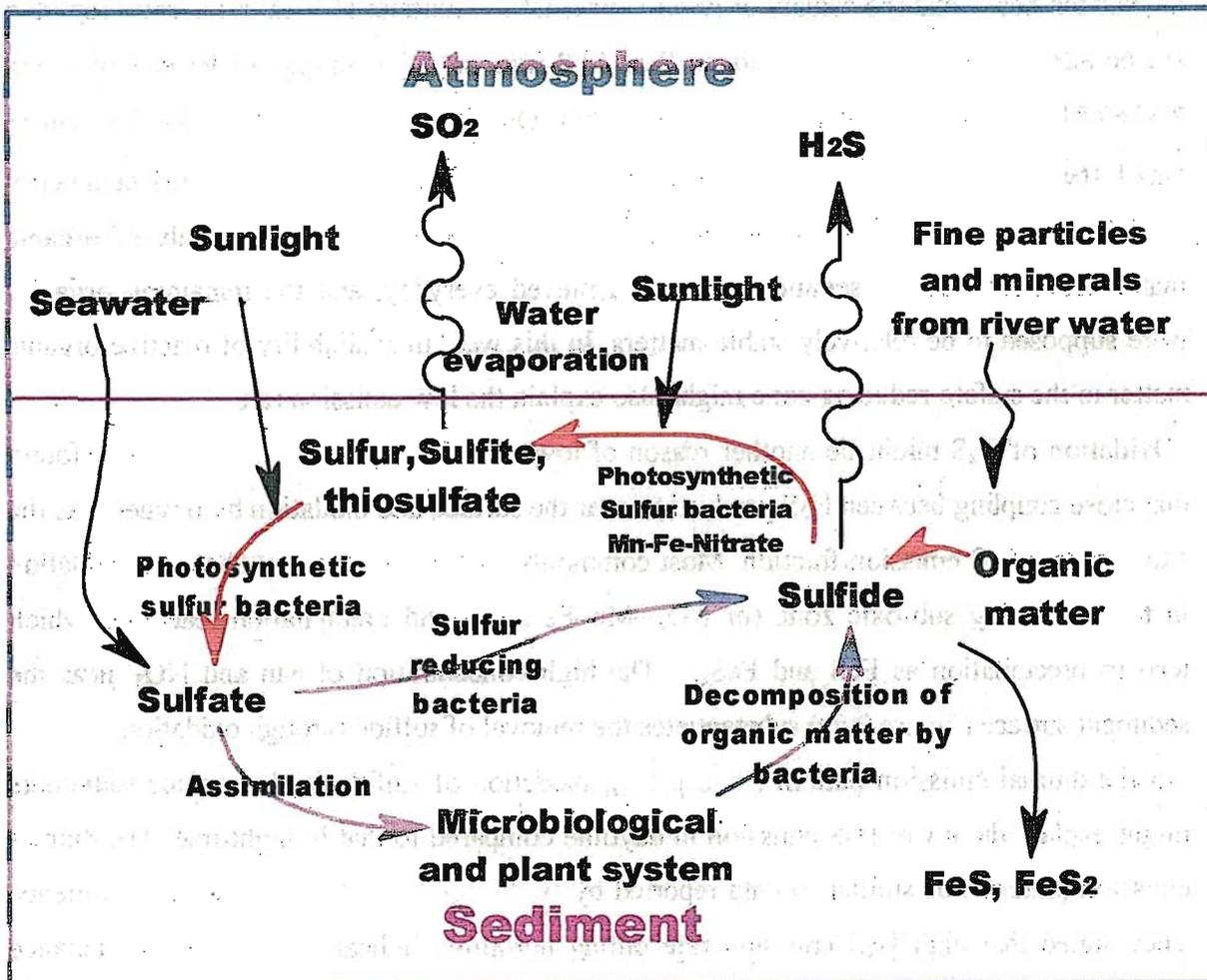


Figure 2.8. Estimated mechanism of H_2S and SO_2 emissions from tidal flat sediments.

2.4.7. Emission of SO_2

As mentioned before, it was found that SO_2 was emitted at both the muddy and sandy sites. Total sulfur emitted from Ariake Sea tidal flat as SO_2 was $19.6 \text{ } 15.5 \text{ t S y}^{-1}$. Interestingly, SO_2 was highly emitted even at neutral sediments. Furthermore, SO_2 was dominant over H_2S at both the muddy and sandy sites during the measurement period. So far, in all investigations on biogenic sulfur gas emission from neutral soil, SO_2 data was not presented. Harrison *et al.*

²⁹ attempted to measure SO₂ together with the reducing sulfur gases, but SO₂ emission was negligible and data were not reported. This might be due to the wet nature of sediments, and the inability of SO₂ to disperse to the gas phase from water or sediments. Just recently, emission of SO₂ from sediments was firstly shown by Macdonald *et al.*²⁰ In that study, Macdonald *et al.* measured acid sulfate soils where pH was around 4. Two decades ago, van Breemen^{33,34} proposed that acids sulfate soils could emit SO₂ directly to the atmosphere. This hypothesis has been demonstrated by Macdonald *et al.* Average SO₂ emission rate calculated from those studies was 111.6 μgS m⁻² h⁻¹. In the Ariake Sea tidal flat campaign, soil was neutral or weekly alkaline, but SO₂ emission was confirmed at the both two sampling sites. Particularly, the sandy site emission averaged 27.8 μgS m⁻² h⁻¹. The average emission rate observed in the sandy site of Ariake Sea tidal flat was quarter of the emission from the acid sulfate soil. Sulfur cycle occurring in sediments and at the boundary to the atmosphere is estimated as in Figure 2.8. Sulfite is an intermediate product of the sulfide oxidation process at the marine sediment surface. It is produced in soils either through an inorganic pathway or biodegradation of organic sulfur compounds such as cysteine sulfinic acid (HOOSCH₂CH(NH₂)COOH).²⁰ Sulfite, which is the origin of SO₂, is formed from oxidation of sulfide by the help of photosynthetic sulfur bacteria with sunlight³⁵ and Mn-Fe-NO₃⁻ oxidation system.³⁰ Sunlight helps the former process. Moreover, irradiation from the sun makes sediments warmer and accelerates water evaporation. The sediment drying process promotes SO₂ emission.²⁰ These are believed to be the reason why SO₂ emission was high in the daytime. In addition, biological activity and water vaporization are high in warmer seasons, and SO₂ emission is higher in these seasons. In bigger grain sediments, oxidation of sulfide is easier due to a higher permeability of oxygen,²⁶ and water evaporation is suggested to be higher. Thus, sandy sediments showed richer in SO₂ emission than muddy sediments.

2.4.8. Total Sulfur Flux to the Atmosphere

Yatsumimi *et al.*³⁶ estimated sulfur emission as H₂S from Japanese whole coast to be < 90 t S y⁻¹. Those authors themselves commented in that paper that the emission value was overestimated because parameters used for the estimation were too big. For example, average tidal width of the whole Japanese coast was assumed to be 100 m, and H₂S data were obtained in a high H₂S emission area where H₂S smell existed. Thus, a more reasonable estimation would be much less than 90 t S y⁻¹ for whole Japan (*e.g.* ~10 or 20 t S y⁻¹).

For Ariake Sea tidal flats, yearly total sulfur flux to the atmosphere as H₂S and SO₂ was estimated from the average seasonal sulfur flux data. These are shown in Table 2. The sandy

site is flooded twice a day. However, only about half of the muddy site is flooded twice a day, and the another half is flooded only by the spring tide. By observing tidal conditions, we concluded that the average emission period from sediments to atmosphere was 12 hours daily being the same as in the estimation by Yatsumimi *et al.*³⁶ Estimated total sulfur turnover in the whole tidal land of Ariake Sea was 20.2 t S y⁻¹. This data for the small closed sea, Ariake Sea, is comparable to sulfur emission from Japanese whole coast estimated from the H₂S emission. This shows that natural sulfur emission in Ariake Sea coastal area contributes largely to the total sulfur turnover, especially contribution of SO₂ is high. Average sulfur emission rate per unit area at Ariake Sea tidal flats was 0.195 t S km⁻² y⁻¹. Yanagawa, Yamato and Okawa cities are situated in the vicinity of Ariake Sea tidal flats. Anthropogenic sulfur emission rates from these towns are 0.18, 0.17 and 0.22 t S km⁻² y⁻¹, respectively. Biogenic sulfur emission from tidal flats significantly contributes to the local atmospheric environment around Ariake Sea.

Table 2.2.
Mean sulfur flux in each sediment and estimation of yearly emission

Sediment	Gas	Emission rate average ($\mu\text{g S m}^{-2} \text{h}^{-1}$)	Yearly (t S km ⁻² y ⁻¹)	Turnover (t S y ⁻¹)
Muddy	H ₂ S	0.68	0.0060	0.18
	SO ₂	6.44	0.0564	1.69
	Total	7.12	0.0624	1.87
Sandy	H ₂ S	0.56	0.0049	0.36
	SO ₂	27.8	0.244	17.9
	Total	28.4	0.249	18.3
Whole Ariake	H ₂ S		0.0052	0.54
	SO ₂		0.189	19.6
	Total		0.195	20.2

2.5. Conclusions

Sulfur fluxes to the atmosphere from tidal flat sediments have been measured in Ariake Sea, Japan. SO₂ is the dominant gas emitted from the tideland compared to H₂S. Emission trends of the two gases are different. H₂S is highly emitted from muddy sediments at nighttime. On the other hand, SO₂ is highly emitted from sandy sediments during the daytime. However, both gases are highly generated in warm seasons. The total amount of sulfur emission (~20 t S yr⁻¹) is significant, which might have adversely impacted on the atmosphere of towns situated in the vicinity of tidal flats, and especially SO₂ is a dominant contributor.

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